PYROLYTIC REFRACTORY MATERIALS

FOR SOLID-FUEL ROCKET MOTOR APPLICATIONS

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Summary Status Report

on

PYROLYTIC REFRACTORY MATERIALS FOR
SOLID-FUEL ROCKET MOTOR APPLICATIONS

By

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ABSTRACT

Results of an experimental program devoted to the development
of refractory materials formed by pyrolytic processes are de-
scribed. In this regard the relative merits of various pyrolysis
techniques and furnace designs are critically evaluated, and op-
timum conditions for the formation of pyrolytic graphite and pyro-
lytic boron nitride have been investigated. Relevant properties of
pyrolytic graphite and pyrolytic boron nitride are compared, and
application of the principles derived has resulted in the formation
of several large sound shapes of these materials. Exploratory
experiments on the formation of other pyrolytic systems are also
described.

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I. INTRODUCTION

Technology in the field of missile development has approached a point where temperatures encountered greatly exceed the limitations of refractory metals. The severe thermal conditions undergone by such devices as rocket nozzles and liners present the structural designer with a materials problem of a type not previously encountered. Materials are required for service at temperatures above 1650°C (3000°F).

In many respects nonmetallic components appear to fulfill these requirements. However, their application has been greatly impeded by certain limiting factors, particularly brittleness and difficulties in fabrication. Present knowledge of ceramic materials is also limited, principally with respect to physical properties, mechanism of fracture, and fabrication of uniform structures. Consequently the field is a broad and important one for investigation.

Much attention is currently being devoted to the development of materials with anisotropic properties as a possible solution to the protection of parts subjected to high heat fluxes. The approach appears to be a valid one. It has long been known that pyrolytically deposited graphite, because of its highly oriented layered crystal structure, exhibits a thermal conductivity along the plane of its surface which is many orders of magnitudes greater than along the axis perpendicular to it. Thus, in this application, pyrolytically formed materials with high melting points, resistance to erosion, and anisotropic in thermal properties potentially could provide thermal insulation to the shell of a rocket motor at temperatures beyond the range of present-day alloys.

The synthetic unit of this program is those compounds of graphitic crystal structure which show marked anisotropic thermal properties. Relatively few such materials exist, but those available show excellent potential as high-temperature structural materials. In the event that no substance exhibits optimum refractoriness, chemical stability, and thermal and mechanical properties, these requirements are to be met by the design of composites or incorporation of modifying additives which will, in combination, yield the desired properties.

This First Annual Technical Summary Report on Contract No. DA-19-020-ORD-5238, covering the period 21 June 1960 to 21 June 1961, summarizes research and development on refractory materials formed by pyrolytic processes for application in solid-fuel rocket motor design. It details the apparatus constructed to perform this program, the experimental procedures developed for preparation of the refractories, methods for property measurement, results, and future plans.

II. SYSTEMS UNDER INVESTIGATION

A survey of the literature has revealed that relatively few refractory compounds are known which possess hexagonal crystal structures and thus offer the possibility of property anisotropy when prepared in well-ordered crystalline form. Of those available, pyrolytic graphite has achieved the attention of a major portion of the research expended, with some interest only recently being directed toward the isoelectronic pyrolytic boron nitride. Of the others which appear to be potentially attractive candidates, little relevant data are recorded, and at best, that available may be considered as only approximate because of the questionable purity of the samples cited.

In the selection of suitable source materials, consideration is preferentially given to: (1) those stable compounds which have suitable vapor pressures at reasonable temperatures, (2) compounds which will react homogeneously, and (3) compounds which will resist the pronounced tendency encountered in this work for vapor decomposition to occur prematurely in the gas injection system rather than at the desired deposition surface, particularly in those instances where a hydrogen gas carrier is required.

A. COMPOUNDS OF GRAPHITIC CRYSTAL STRUCTURE AS HIGH-TEMPERATURE STRUCTURAL MATERIALS

1. Pyrolytic Graphite and Boron Nitride

Pyrolytic graphite is a polycrystalline form of graphite, deposited from carbonaceous vapors when pyrolytically decomposed on a suitable substrate at temperatures of 1500°C to 2500°C[1]. It is a hard, dark-gray, metallic-like material which approaches the theoretical density of graphite. Comparable shapes of tungsten and pyrolytic graphite show a weight ratio of 65/2, and above 2000°C it has the highest strength-to-weight ratio of any material now considered practical for use. A tensile strength value of 45,000 psi above 2800°C compares with the value of less than 1,000 psi for tungsten, one of the better known high-strength materials, and flexural strength values approximate 25,000 psi in contrast to normal graphite which typically ranges from 1,000 to 8,000 psi. Because of the high density of pyrolytic graphite, a 1-mil thickness is impervious to liquids and gases; in addition, as a result of very low chemical activity, it is more resistant to oxidation than conventional graphite. Thermal conductivity values equal to that of copper are exhibited in the plane horizontal to that of deposition while values that are orders of magnitude less occur in the vertical plane. Equally important, the characteristics of pyrolytic graphites are dependably reproducible.

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Boron nitride, which is isoelectronic with graphite, also possesses the graphite crystal structure. The properties and preparation of the pyrolytic boron nitride from ammonia-boron trichloride, borazole, and B-trichloroborazole, as well as pyrolytic graphite from hydrocarbons, will be considered at later points in this report.

2. Diborides of the Transition Metals

In several respects the borides constitute a unique class of compounds for which a detailed knowledge of properties at present is lacking. The paucity of property data is repeatedly cited in the literature. As a group the borides are characterized by high melting points, extreme hardness, and nonmetallic nature. Sufficient research has been done however to indicate that even above 1650°C these materials have excellent strength and oxidation resistance and can be used under conditions and at temperatures where graphite and refractory metals will oxidize. In addition to the characteristics of being highly refractory, strong, hard, and oxidation resistant, the borides have high electrical conductivity, low thermal expansion, and good thermal conductivity. Their excellent chemical stability implies that they can be used in contact with other refractory materials with only slight reaction at high temperatures[2].

The composition, structure, and some of the chemical properties of the metal borides have been studied by Moers[3,4]; Hagg[5]; Norton, Blumenthal, and Sindeband[6]; Sindeband[7]; Brewer, Sawyer, Templeton, and Dauben[8]; Kiessling and co-workers[9,10]; and a few others. In general, data have been obtained on products fabricated by molding and sintering or by hot-pressing techniques. The purity of such products is usually greater than 97 percent, but very little has been done with high-purity materials. Consequently, research and development have been inadequate to evaluate the full potential of these compounds as structural materials.

The diborides of groups 4A, 5A, and 6A of the periodic classification are among the few compounds whose structure bear a relation to that of graphite. In these materials there are alternate layers of metal and boron atoms normal to the c-axis, each metal atom having twelve equidistant boron neighbors, while in the boron plane the atoms are hexagonally analyzed. According to Kiessling[9], the various types of metal boride structures are characterized by the progressive formation of boron strings, chains, double chains, hexagonal nets, and three-dimensional boron frameworks in which boron-boron bonding exists. The three-dimensional framework and hexagonal nets result in a lattice through which the valence electrons of the metal atoms and, at high temperatures the metal atoms themselves, can diffuse freely[11]. Such hexagonal structure, particularly in those compounds where the boron-boron distance is considerably less than that of the metal-boron, suggests a possibility of anistropic physical properties, much as occurs in pyrolytic graphite.

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In order to utilize these unique combinations of characteristics, we have attempted to ascertain to what extent this predicted anisotropic behavior enhances the utility of pyrolytically formed refractory borides of hexagonal crystal structure. The preparation and properties of these borides are considered below.

Direct boride deposition is most readily carried out by hydrogen reduction of the mixed, vaporized chlorides of boron and the desired metal component at a heated surface. This method was first used by Moers[3] and has been investigated more recently by Walther[12] and Powell, Campbell, and Gonser[13], Van Arkel[14] and Becker[15, 16] have reviewed the early work.

It is also feasible that such borides as Ti, Zr, Hf, and U may be directly deposited by the thermal decomposition of the corresponding borohydrides, although this method has not received much study. The borohydrides are easily prepared by metathesis with lithium and aluminum borohydrides[17], and the vaporization temperatures required for these materials are conveniently in the 20°C to 50°C range.

Data on the high-temperature stability of the borides are scarce, but Kiessling[9] has shown evidence that those of the transition elements are similar to the hydrides, carbides, and nitrides of these elements, in which stability decreases with increasing atomic number of the transition element within the period. However, the borides are much more resistant to oxidation than the above compounds. In air, boron and the borides resist oxidation up to 1200°C-1300°C, although superficial oxidation occurs at lower temperatures. Vanadium diboride is oxidized at an appreciable rate at 1000°C to 1100°C and tantalum and tungsten borides at 1100°C to 1200°C. On the other hand, zirconium diboride is reported to be fairly resistant up to 1300°C or 1400°C, and titanium diboride up to 1400°C or 1500°C, although some oxide film is formed at these higher temperatures. In addition, Cooper Metallurgical Associates reports, that the borides of aluminum, silicon, and chromium also resist oxidation at high temperatures.

In general, little information on tensile, compressive, bending, impact, and stress rupture strength, as well as the effects of temperature on these properties, is available, and some of the data reported are questionable. On the basis of recent determinations on titanium diboride, the strength-weight ratio is not exceeded by any other bulk material from 1600°C to above 2000°C. Attention is called to its extreme hardness.

The flexural strength of titanium diboride (96 percent theoretical density) has been found to be 35,000 psi from 25°C to 2000°C with a modulus of elasticity of this product of 60×10^6 psi. The compressive strength measured by other investigators has been reported as 97,000 psi at room temperature. For the zirconium compound modulus of rupture values are reported from 8,000 to 29,000 psi at room temperature. These are inconsistent with a tensil strength value in the literature of 28,700 psi. Modulus of elasticity is reported at 50×10^6 psi at room temperature. Few other values are available.

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Thermal conductivity data near room temperature show values of 0.03 to 0.06 cal cm sec^{-1} with a positive temperature coefficient for the diboxides of titanium, zirconium, tantalum, and niobium. The borides are good conductors of electricity, often orders in excess of the parent metal. No information on the anisotropy of these properties is published.

The thermal expansion coefficients of zirconium and titanium borides have been reported as 7.3×10^{-6}/°C and 8.1×10^{6}/°C to 1000°C, respectively. Melting points of ca. 3000°C are not uncommon.

There has been no systematic consideration of the thermal shock properties of the borides, but in view of the thermal and mechanical characteristics, the borides might be expected to have relatively good thermal shock resistance when compared with other ceramic materials. In the present state of the art, they would not, however, approach the thermal shock resistance of the metals. Certain physical properties of these diborides are listed in Table I.

3. Hexagonal Nitrides, Carbides and Silicides

Hexagonal molybdenum carbide, Mo_2C, is reported to form by the thermal decomposition of molybdenum carbonyl at reduced pressure in a continuous flow system although the carbide of molybdenum obtained is highly dependent on the substrate temperature and carbonyl pressure, the geometry of the plating chamber and specimen, and upon the rate of gas flow[18]. Adherent, cubic Mo_2C deposits have been formed from 350-475°C and at carbonyl pressures of 0.01 to 0.2 mm of mercury. However, as the temperature and pressure increase, the deposits were shown to contain increasing percentages of hexagonal Mo_2C. Pring and Fielding[19] have made the compound by heating the carbon rods in $MoCl_4$ or $MoCl_5$ atmospheres at 2 mm mercury pressure and below. At a specimen temperature of 1280°C, a bright molybdenum metal coating was obtained; at 1330°C, a mixture of metal and carbide was deposited, while at 1480°C and 1600°C, only Mo_2C was formed. Solid solution of carbon in Mo_2C was noted. An alternate procedure is the reduction of molybdenum pentachloride with hydrogen in the presence of methane as possibly a more suitable source of Mo_2C, a reaction known to occur at 800°C and possibly higher[20].

Physical property data on this compound are sparse and again questionable. For example, the modulus of elasticity at room temperature is variously reported as 12.4 to 77.4×10^{-6} psi. The melting point is given as 2690°C.

The tungsten analog is not full characterized. Nitrides of molybdenum, tantalum and chromium and disilicides of molybdenum, vanadium and chromium also exhibit hexagonal crystal structure. Whether these compounds when prepared in ordered crystals would display property anisotropy is again, at best, debatable. However, in solution with graphite, their refractory nature would undoubtably lend attractive properties to the composite.

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TABLE I

PHYSICAL PROPERTIES OF BORIDES OF HEXAGONAL CRYSTAL STRUCTURES

Boride	Density g/cc	Hardness Knoop (100g) kg/mm^2	Melting Point °C	Room Temperature Thermal Conductivity cal/cm^2 sec°C	Room Temperature Electrical Resistivity microhm-cm
CrB$_2$	5.60	1,800	1,850	-	21
MoB$_2$	7.80	1,280	2,100	-	40
CbB$_2$	7.20	2,595	2,900	0.040	32
TaB$_2$	12.60	2,537	3,000	0.026	68
TiB$_2$	4.40	3,400	2,900	0.062	15
UB$_2$	12.71	1,390	2,365	-	-
VB$_2$	5.28	2,800	2,100	-	16
WB$_2$	-	2,660	-	-	-
ZrB$_2$	6.10	1,750	3,040	0.055	9 - 11
HfB$_2$	11.20	-	ca. 3,000	-	10

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B. COMPOSITES

Portions of the investigation have been directed toward the development of combinations of pyrolytic graphite with other structurally related compounds and toward such other materials as are capable of being formed by techniques similar to those employed in the production of pyrolytic graphite. It is desired that these materials possess the oriented layer crystal structure and thermal anisotropy exhibited by pyrolytic graphite.

A great number of volatile compounds are available that may be used in admixture with hydrocarbons and subjected to vapor phase decomposition. Any such combinations that would reduce the volatility of graphite and enhance its chemical stability would be of very great value in permitting better utilization of its refractory properties. Graphite has the highest melting point of any substance known.

Because of the similarity in crystal structure and lattice dimensions of the compounds discussed in Section IA, these compounds will enter into considerable solid solution with each other when formed from the vapor phase. Materials other than those of hexagonal crystal structure may also enter into solid solution or bond formation with them provided the lattice dimensions are not totally unfavorable.

1. Pyrolytic Composites of Compounds with Hexagonal Crystal Structure

Compounds of the hexagonal crystal system are expected to undergo extensive solid solution when prepared by simultaneous pyrolysis of appropriate source materials from the vapor phase, and by way of example, we can speculate that a composite of pyrolytic graphite and pyrolytic boron nitride may result in the following properties:

1. Enhanced stability of the composite over either of its components. Boron nitride is more resistant to oxidation than graphite at temperatures of 1000°C and somewhat higher, while graphite is the more refractory material (sublimation temperature: boron nitride 3000°C; graphite 3600°C).

2. Pyrolytic graphite-boron nitride combinations may result in enhanced hardness over pure pyrolytic graphite.

3. With respect to mechanical properties, it is anticipated that a combination of boron nitride, having high mechanical strength at low temperatures, where graphite exhibits relatively low strength, would be advantageous. At higher temperatures the loss of strength of boron nitride might be compensated in part by the increased strength with temperature of graphite.

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4. It is reasonable to expect that the inferior thermal conductivity of boron nitride would be compensated for by graphite in the composite.

5. The emissivity of the boron nitride-graphite combination will be higher than that of boron nitride alone.

In addition to the formation of such composites by simultaneous deposition of several source materials, the pyrolytic deposition of such compounds as hexaphenylborazole, triphenylborazole, triphenylboroxide, and members of these series, easily prepared by Grignard reaction, appears to offer a closer control over the ratio of components in the product and may reduce any tendency toward preferential deposition.

2. Molybdenum Disilicide

Molybdenum disilicide has wide use as high-temperature, refractory, wear-resistant material; the formation of composites of the compounds discussed in Section IA with molybdenum disilicide is considered to have useful potentialities. Unlike those compounds, molybdenum disilicide is an example of a compound which crystallizes in the tetragonal system, but whose lattice constants are not so far removed to preclude the possibility of solid solution when formed by simultaneous deposition. Unpublished data of The Carborundum Company have shown that a marked improvement in oxidation resistance is obtained from a body made of 90 percent zirconium boride and 10 percent molybdenum disilicide, while thermal cycling tests on a 90-10 $ZrB_2 \cdot MoSi_2$ composite showed a 50 percent increase in strength after 30 cycles from room temperature to 1350°C with cooling in an air blast, whereas an alumina specimen failed at 2 cycles.

3. Pyrolytic Boron Silicide

Boron-silicon combinations have been shown to have excellent thermal shock and oxidation resistance[21, 22]. Their pyrolytic formation, with codeposition of pyrolytic graphite from mixtures of silicon and boron halides offers a potentially interesting possibility.

4. Pyrolytic Borocarbons

A class of materials that have been designated as borocarbons by investigators at the Bell Telephone Laboratories[23] are combinations which are considered to be solid solutions of boron in carbon, with the stoichiometric compound B_4C being formed at high temperatures.

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Investigations of the properties of carbon shortly after the turn of the century indicated that they could be greatly modified by the addition of boron. Boron, because of its very small atomic radius, is particularly suited for incorporation into the pyrolytic graphite structure, and this may be readily accomplished by pyrolysis of a single compound such as tripropylborane or by use of a mixture of a boron halide and a hydrocarbon. In this manner, the Bell Telephone Laboratories reported early in 1951 of preparing samples containing up to 25 percent of boron. In recent work, however, the Raytheon Company reported the incorporation of 2.7 percent of boron in pyrolytic graphite[24]. This work is being performed at high (>2000°C) deposition temperatures in order to obtain pyrolytic graphite which is well ordered in structure and approaches theoretical density, but a high vapor pressure, boron exhibits thus rendering deposition difficult. The 25 percent saturation is also highly suggestive of compound formation and not simple solution.

5. Metal Additions

It is interesting to speculate as to the effect of incorporation of small percentages of metal atoms into the structures of pyrolytic graphite, boron nitride, etc. This may, in general, be accomplished by pyrolysis of mixtures of volatile metal halides with hydrocarbons in a reducing (hydrogen) atmosphere. Because many metal halides have low vapor pressures, even at 200°C, and require the hazardous use of hydrogen gas in large quantities, a survey of selected organometallic compounds has been made to determine possible advantages offered by them. Ideally, pyrolysis might give pyrolytic graphite alloys directly but even failing this, they may serve as improves sources of metal incorporation. Attention is focused on those systems where carbide formation is least likely to occur.

The first member of a remarkable series of organometallic compounds was obtained in 1951 when attempts to prepare dicyclopentadienyl were made by treating cyclopentadienyl magnesium bromide with ferric chloride[25]. The reaction of Grignard reagents with transition metal halides is known to be a satisfactory method of preparing hydrocarbons, the success of the reaction being essentially due to the instability of normal organic derivatives of the transition elements. In this particular case, however, the reaction failed to produce dicyclopentadienyl but resulted in the formation of biscyclopentadienyliron or "ferrocene," a yellow crystalline compound of then unique structure and unusual stability. The discovery of the cyclopentadienyl metal compounds has accompanied a vigorously renewed effort in the field of organometallic chemistry which has led to the preparation and characterization of a great number of new organoaluminum, organosilyl metallic, vinyl metallic, olefin and acetylene derivatives, alkyl, aryl, and arene compounds and derivatives of transition metals. Although many of these novel compounds may have practical interest in the present application, all of them, however do not share such attractive properties of ferrocene as ease of preparation and handling, stability at 400°C, and vapor pressure of 10 mm at 100°C.

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The reactions of cyclopentadienylsodium and a metal halide in tetra-hydrofuran or cyclopentadienyl with a metal carbonyl at 360°C are a means of preparing the compounds listed below, many of which are considered to be of immediate interest:

$(C_5H_5)M$ M = Ti, V, Cr, Mn, Fe, Co, Ni

$(C_5H_5)MX_2$ M = Mo, Ti, V. X = halide

$(C_5H_5)MX_3$ M = Nb, Ta. X = halide

$(C_5H_5)_a M_b(CO)_c$ M = Ti, V, Cr, Mn, Fe, Co, Ni, Mo, W.
          a = 1, 2. b = 1, 2. c = 2, 3, 4, 6.

Several excellent reviews summarize the salient properties of the numerous compounds available. [26, 27, 28, 29, 30]

Dicarbonyl compounds have been known for many years to form stable complexes with metal ions. Of the dicarbonyl compounds investigated, acetyl-acetone (2,4-pentanedione, I) has received the most attention. Because of its ability to enolize to the acid form (II), this diketone will, in general, react readily with metal ions in the presence of base to produce the familiar thermo-dynamically stable six-membered chelate ring system.

       I   II
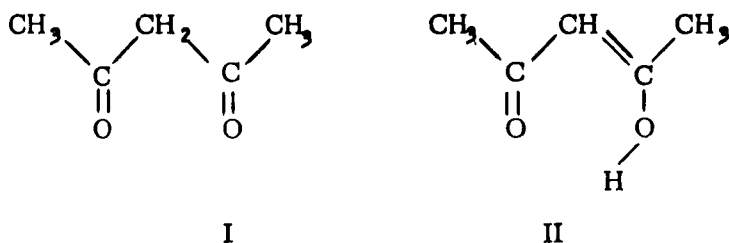
If the charge in the metal ion entering into complex formation is one-half its coordination number, then nonelectrolytic inner complexes are formed, including $Be(AA)_2$, $Cr(AA)_3$, $Th(AA)_4$ (where $AA = C_5H_7O_2^-$), with the typical covalent properties of solubility in nonpolar solvents, volatility, etc. If the coordination number of the central ion is less than twice its charge, relatively nonvolatile cationic compounds are formed, for example, $[Ti(AA)_3]_2 TiCl_6$. Similarly, anionic complexes such as $KCo(AA)_3$ can also be obtained.

Compared to all other metal chelate compounds in which the complexing organic molecules possess relatively simple structures, the metal acetylacetonates are uniformly the most stable, physically and chemically. The Cr(III) and Be(II) boil at atmospheric pressure without decomposition. Many acetylacetonates are readily sublimed at temperatures to 300°C.

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Although it is recognized that the metal-oxygen bond may prove to be an undesirable feature of these compounds, the following are also potential sources for incorporation of metals into the pyrolytic graphite structure:

$M (C_5H_7O_2)_2$ - Fe, Co, Ni, Be, Ti, Mn

$M (C_5H_7O_2)_2$ - V, Cr, Mn, Fe, Co

$M (C_5H_7O_2)_4$ - Zr, Th, Hf

$M O_2(C_5H_7O_2)_2$ - Mo
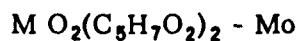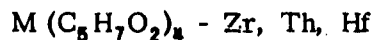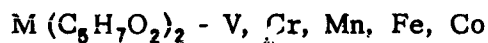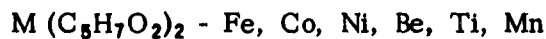
6. Layered Deposits

Structures in which the components are pyrolytically deposited in alternate layers are of considerable interest. Anisotropic thermal properties and corrosion resistance will be enhanced in a deposit consisting of alternate layers of pyrolytic graphite, for example, and of some other pyrolytic material or of a suitable metal oxide.

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III. VAPOR DEPOSITION APPARATUS

   The method used for preparing pyrolytic materials is very simple conceptually, as it consists merely of flowing appropriate materials as vapors past a hot surface where pyrolysis and deposition may occur. However, the process is very complicated fundamentally, and a complete characterization of this process requires that temperature, pressure, flow rate, geometry, diffusion coefficients, and rate constants for all reactions as well as thermal conductivities and accommodation coefficients for gaseous species be known. Fortunately, an empirical approach may be taken, and it appears that the major parameters are temperature, flow rates, furnace geometry, and of course the starting raw material. While temperature is generally considered a most important parameter, it is to be emphasized that the others are at least as important. Consequently, for each system considered, one must critically evaluate the effects of these variables upon sample properties in order to establish optimum conditions for the preparation of pure, uniform, and sound deposits.

   In order to perform screening experiments to establish optimum conditions for deposition and to prepare small samples of pyrolytic materials we designed a glass vacuum system in which an appropriate gas mixture could be passed over an inductively heated graphite substrate. (Figure 1). The system contains: (1) a number of flasks which serve as reservoirs and vapor generators, (2) a mixing chamber, not clearly visible in the photograph, (3) a vertical quartz tube extending through the axis of the induction heating apparatus, (4) cold traps for removing unreacted source material and by-products, (5) 1.5 kw Radio Frequency power supply, (6) micro-optical pyrometer sighted through a mirror system onto the substrate surface (not shown), and (7) vacuum pump (not shown). The entire system may be isothermally heated by electrical heating tapes and is monitored by a series of thermocouples. A General Electric standard lamp was used in the calibration of the micro-optical pyrometer for a temperature range from 950° to 1800°C. Readings were first made by sighting the pyrometer from its fixed operating position through air onto the filament of the lamp as reflected in a mirror held at 45° from vertical. We then made further readings by sighting the pyrometer against the image of the filament as reflected by a 45° mirror at the bottom of the furnace tube and passing through a path consisting of air in the furnace tube, the optical flat at the top, and a second 45° mirror. For a constant current through the filament of the tungsten lamp and corresponding to a given temperature, the differences in temperature readings were due to the difference in optical path caused by the presence of the optical flat and the upper mirror. The corrections in the form of calibration curves enable the temperature to be determined with an error of less than 1 percent at 1800°C.

   It should be noted that a complication arises in optical pyrometer measurements of the temperatures of the graphite button as it becomes coated with a pyrolytic deposit. This, of course, results from the difference in emittance

12
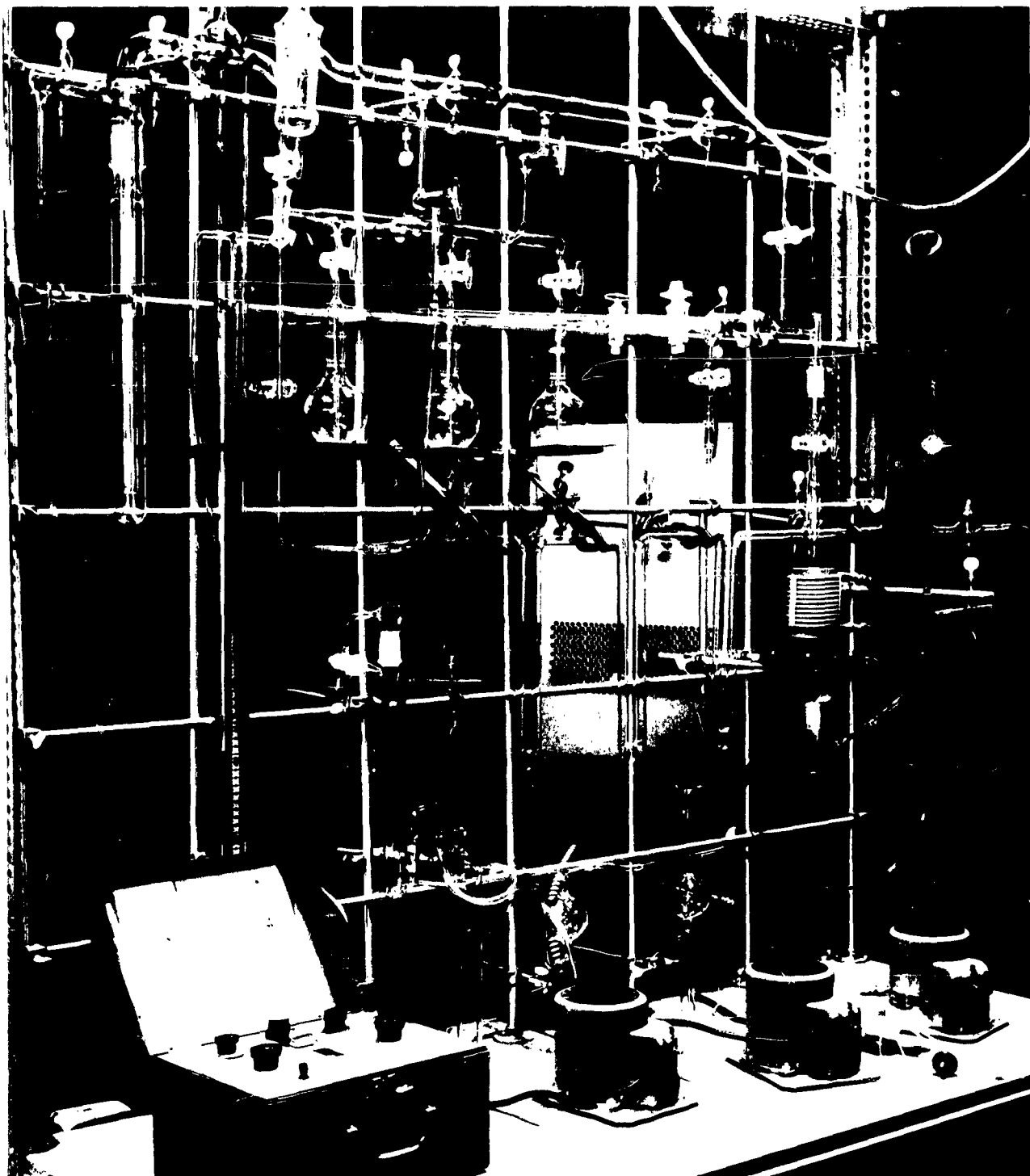
FIGURE 1   Glass Vacuum System and Furnace for Preparation of Pyrolytic
            Samples

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properties exhibited by various materials. For example, boron nitride is an excellent reflector of radiation; whereas, graphite shows strong absorption. We have made spectral emittance measurements[41] of massive boron nitride at various temperatures over the range from 2 microns or less up to 14 microns. The values at low wavelengths are shown in Table II. Extrapolation of the spectral emittance curve at 1080°C to 0.65 microns, the wavelength for which the optical pyrometer is calibrated, gives an emittance at this wavelength of 0.21 ($\pm$ 10 percent). Equipment is not presently available for measuring emittance at temperatures in the range of 1600° to 2000°C, with which we will be principally concerned; but assuming that the emittance remains constant to those temperatures as it does in the 600° to 800°C range, for low wavelengths, a value of 0.2 for the emittance of boron nitride at 0.65 micron may be estimated. The validity of the assumption of constant emittance for boron nitride at low wavelengths is open to some question, however, since the spectral emittances of "black" materials, e.g., silicon carbide and, to a lesser extent, graphite, are strongly temperature dependent.

It is not unusual then to observe a change in susceptor temperatures amounting to 100° to 200°C that may be only apparent because of a difference of emissivity or real because of a change in the electrical characteristics of the radiating surface.

Although a detailed consideration of this problem is thought to be beyond the immediate requirements of the program, a simple solution is to drill a cavity into the center of the graphite substrate into which the pyrometer can be sighted. The cavity must have a depth of three to four times its diameter to approximate black-body conditions, but the diameter must be sufficient so that the cavity will not be filled by the deposit before the temperature stabilizes.

The furnace design is a modification of a Sylvania Induction lamp, diagrammed in Figures 2 and 3. In the Sylvania equipment, a power supply provides high voltage dc which is converted by radio frequency generator to high frequency ac (about four megacycles). The radio frequency generator is coupled by means of an induction coil with a water-cooled concentrator surrounded by a Pyrex glass envelope. A slit in the concentrator forces the magnetic flux to concentrate about a tantalum carbide target which can be heated to temperatures in the region of 3700°C.

This lamp has been modified to suit the present purpose. The tantalum carbide susceptor has been replaced by a graphite disc, which is surrounded by a quartz tube through which vapors pass to be pyrolyzed and deposited on the hot susceptor.

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TABLE II

SPECTRAL EMITTANCE DATA OF BORON NITRIDE

Temperature °C	Wavelength Microns	Emittance
600	2	0.33
810	2	0.32
1,080	2	0.32
1,080	1.5	0.255

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GLASS ENVELOPE

TARGET

R.F. POWER
SUPPLY

INDUCTION
HEATING
COIL

GLASS ENVELOPE

TARGET

CHARGE
CONCENTRATOR

CHARGE
CONCENTRATOR

WATER COOLING
TUBES

FIGURE 2   Sylvania Induction Lamp

16

3"

$\frac{5}{8}$

SAMPLE

SHELF AT END OF
FINGERS TAPERED
TO INSURE MINIMAL
THERMAL CONTACT
WITH SAMPLE

3 FUSED
MAGNESIA FINGERS

SILVER PLATED
COPPER CHARGE
CONCENTRATOR

2 QUARTZ-PYREX
GRADED SEALS
JOINED QUARTZ
TO QUARTZ

COOLING COILS

R-F HEATING COILS

TEFLON SCREWS

3"

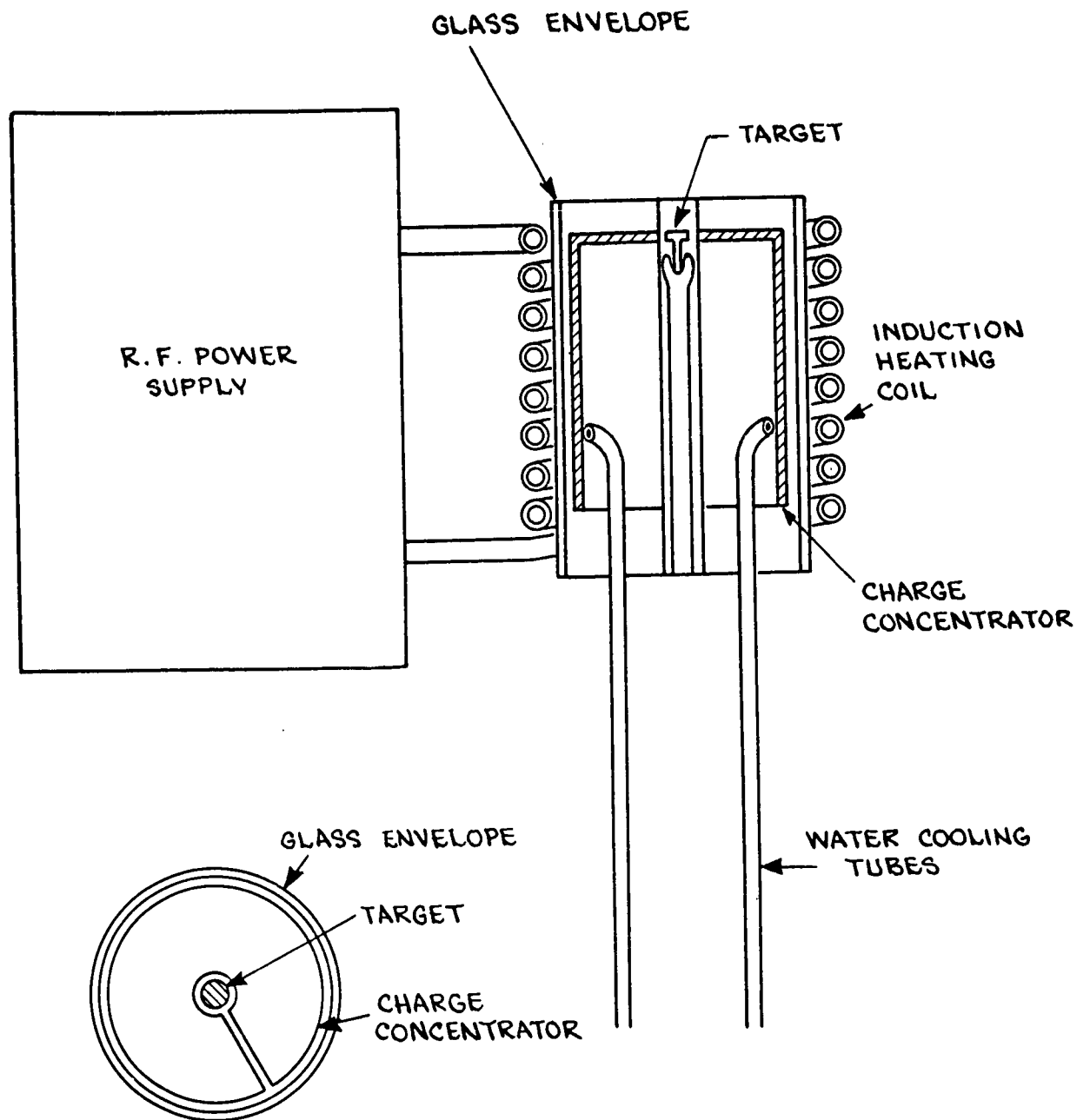STAINLESS STEEL SPRINGS
UNDER COMPRESSION

COOLING WATER

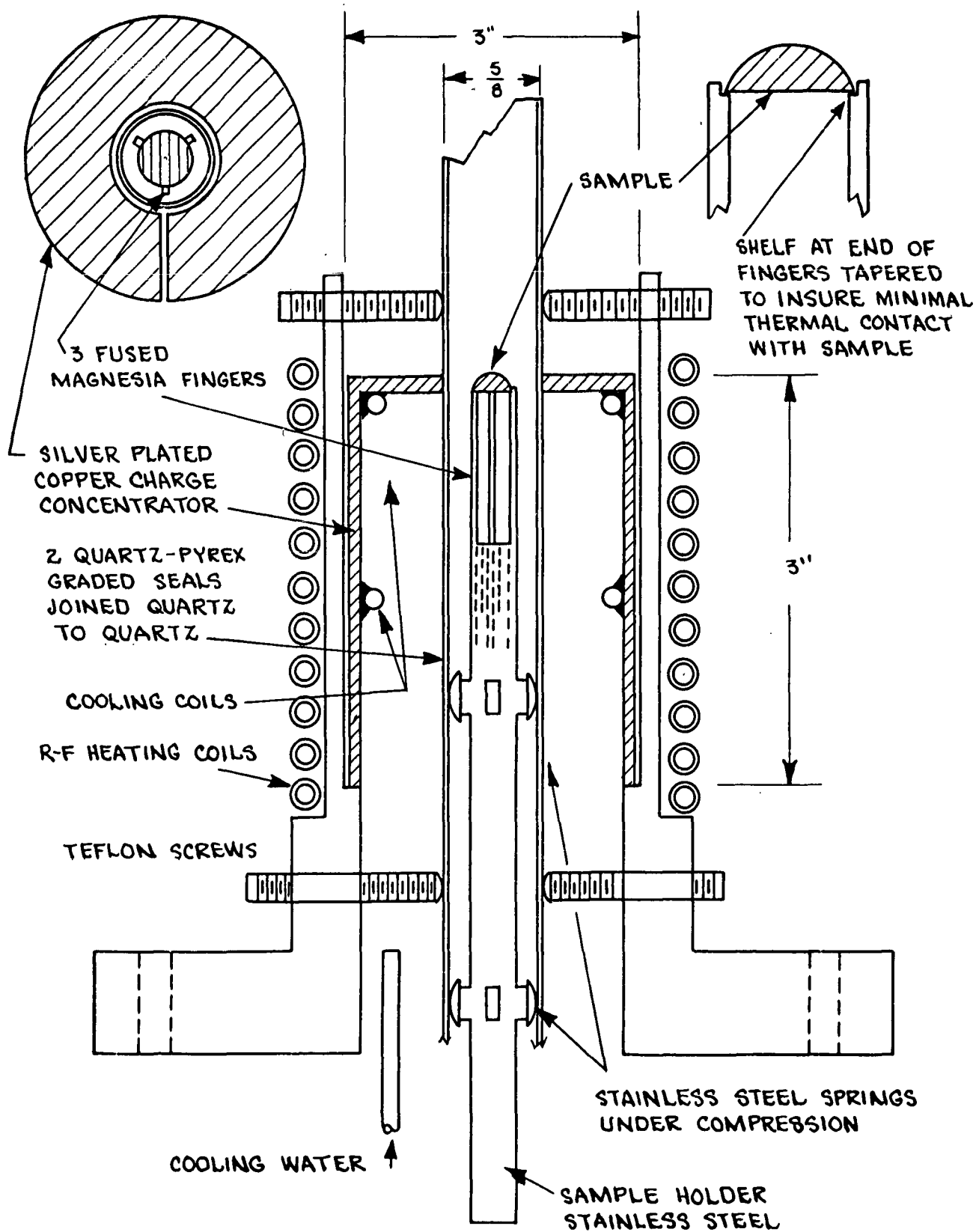SAMPLE HOLDER
STAINLESS STEEL

FIGURE 3   Susceptor Support Scheme

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Not only is the maximum obtainable temperature in this system dependent on the material of which the susceptor is composed, but the temperature also falls off rapidly as the distance between the susceptor and the charge concentrator increases. In order to determine an optimum concentrator opening, a series of experiments has been performed[31] in which a TaC target was employed in a charge concentrator drilled out in three stages and interposing successively wider bore silica tubing. The results are shown in Table III. The target diameter in every case was 0.321 inch, and an argon atmosphere was used. The silica showed no evidence of melting even at the smallest clearance between the furnace wall and susceptor.

As the graphite susceptor on which the pyrolytic material is to be deposited must be of appreciably smaller diameter than that of the furnace wall to prevent blocking of the gas stream as the deposit grows, the experiments have had imposed upon them a temperature limitation of approximately 1700°C.

In order to obtain higher temperatures and to produce larger pyrolytic shapes, an induction furnace unit has been constructed containing a 4- by 8-in. fused quartz furnace cavity. The vacuum system is essentially a simple scale-up of that previously described. The vapor stoichiometry is again controlled by temperature and, after suitable mixing, is pumped over the inductively heated substrate. The quartz furnace is flanged and slotted and is mounted to the remainder of the system through O-rings to a Pyrex copy. The entire assembly is mounted in a 7- by 6- by 2-foot walk-in hood with power supplied by a Radio Frequency Company 450 kcs, 30 kw., R.F. generator. The most suitable work coil design for inductively heating large carbon substrates has not been determined, but a small four-turn element was used to melt a sample of impure zirconium carbide at 3400°C.

Induction heating is adequate for the general requirements of this program and, in fact, offers a number of advantages over resistance heating. Among the advantages are relative ease of apparatus set-up, cleaning, and maintenance that are due to simplicity of design; the higher temperatures and more rapid and concentrated heating afforded; the elimination of complex injector-substrate geometry considerations provided by the simple gas injection system; absence in the furnace hot zone of electrical connections which require water cooling and which are subject to reaction with the corrosive gases introduced promoting product contamination; ease of adaptation of a single power unit to a variety of furnace designs; and visual observations of the experiment. Induction heating does however, suffer from two critical drawbacks. As implied previously, there is a limit to the size of the susceptor which may be heated, and a material must obviously be an electrical conductor in order to respond appreciably to the electromagnetic field in which it is placed. Consequently, a major portion of this investigation of necessity was devoted to the alternative approach.

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TABLE III

TEMPERATURES REALIZED AT VARYING FURNACE GEOMETRIES IN THE MODIFIED SYLVANIA INDUCTION LAMP

Furnace LD (in.)	OD (in.)	Concentrator Diameter- Original 0.375 (in.)	Voltage Setting	Temperature °C	Higher Temperatures Possible
0.343	0.447	0.453	2,200	2,000	Yes
0.466	0.576	0.590	3,200	2,000	Yes
0.587	0.731	0.734	3,500	1,700	No

To this end a high-temperature vacuum graphite-resistance furnace, as supplied by Vacuum Specialties Company, Somerville, Massachusetts, and shown in Figures 4 and 5, has also been employed to produce large pyrolytic shapes and for process study. The furnace unit consists of a water-cooled steel shell which contains as a heating element a 4- by 8-inch slotted graphite tube surrounded by appropriate insulation and radiation shields.

In early trials a temperature of 2800°C was reached with this unit requiring a power input of about 20 kva, and in another the temperature was maintained at 2400°C over a period of 9 hours with the maintenance of a vacuum of under 200 microns. However, in these experiments there was no gas injector present, which increases somewhat the power requirements of the furnace. The power supply is housed in a steel cabinet 7 feet wide, 5 feet high, and 3 feet deep, along with a 30 cfm Kinney KD-30 pump and several auxiliary devices. The furnace itself projects about 2-1/2 feet beyond the cabinet front.

The uniformity of thickness of a deposit built up on a substrate by the thermal decomposition of a gas during any given experiment depends chiefly on two factors--the geometrical relationships of the inlet tube of the injection system to the surface being coated and the rate of gas flow. For a given flow there is an optimum design position of the injector tube that will give maximum uniformity of deposition. The objective is to obtain as uniform a flow of gas as possible to all parts of the surface, taking into account the effect of gaseous products released by the decomposition. Producers of the pyrolytic graphite have expended much effort in calculating the flow of gas over various shapes. To this point in our program, no attempt has been made to control the thickness of the deposits precisely, and a simple injector design has been used.

The injector, as shown in Figure 6, will deliver vapors into the furnace to within 1/4 inch of the deposit substrates. It consists essentially of two concentric brass tubes, the inner being used for delivering the vapor, and the outer being divided into two chambers so that the flow of cooling water will be directed with maximum force and turbulence at the hottest part of the tube. With this design, we calculate that a flow rate of 2-5 gallons per minute at 210 psi will cool the injector so that the temperature of the outlet water will not exceed 120°F. The temperature of the injector is carefully measured by a thermocouple welded as part of the wall of the delivery end. It is encased in a ceramic and passes up through the water zone and out the top. Three such injectors of two sizes have been employed.

The water pressure through the injector is maintained by a turbine booster pump driven by a 2 hp motor. Provision must be made to cut off the water supply in case the injector fails while the furnace is hot. Two Jamesbury solenoid valves, actuated by a thermoswitch, shut off the water and prevent it from being sucked back into the furnace should the temperature of the outlet water exceed 180°F. In case of

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power failure and melting of the injector, a manual reset switch incorporated in the water pump motor circuit prevents water from being pumped into the hot furnace. It is encouraging to note that, in the one failure sustained, the safety features functioned perfectly.

Monel flasks, used for containing source material, are connected through standard taper joints and Monel vacuum valves with stainless steel tubing and lead to the gas injection system. Condensation in these lines is avoided by electrical heating tapes controlled by variacs.

In order to protect the mechanical pump which maintains the system under vacuum from the corrosive by-products of pyrolysis, a stainless steel trap has been constructed and installed in the system. The top section of this trap has a machined flange drilled for six bolts and consists of a 1-3/4 in. center tube with a 4-in.-diameter housing containing two outlet valves for releasing vacuum in the isolated trap and for isolating the trap on the pump side. The bottom section is 4 in. in diameter and 15 in. long and has a machined flange fitted with an O-ring and drilled to fit the top. The length is important in order to avoid embrittlement of the O-ring seal from the low temperatures given by the liquid nitrogen coolant. Provision is also made to heat the upper part of the trap with a heating tape in order to protect the seal. The trap is fitted with a tubular copper spiral, which provides a long path for cooling of condensible by-products.

Despite the most careful precautions, damage is often sustained by the vacuum pump, and as its isolation for examination has been a time-consuming maintenance job, it seemed desirable to separate it from the remainder of the system by a vacuum valve. A thermocouple gauge has been installed in the system adjacent to the pump so that, with this valve and others existing in the system, sections may be isolated for inspection.
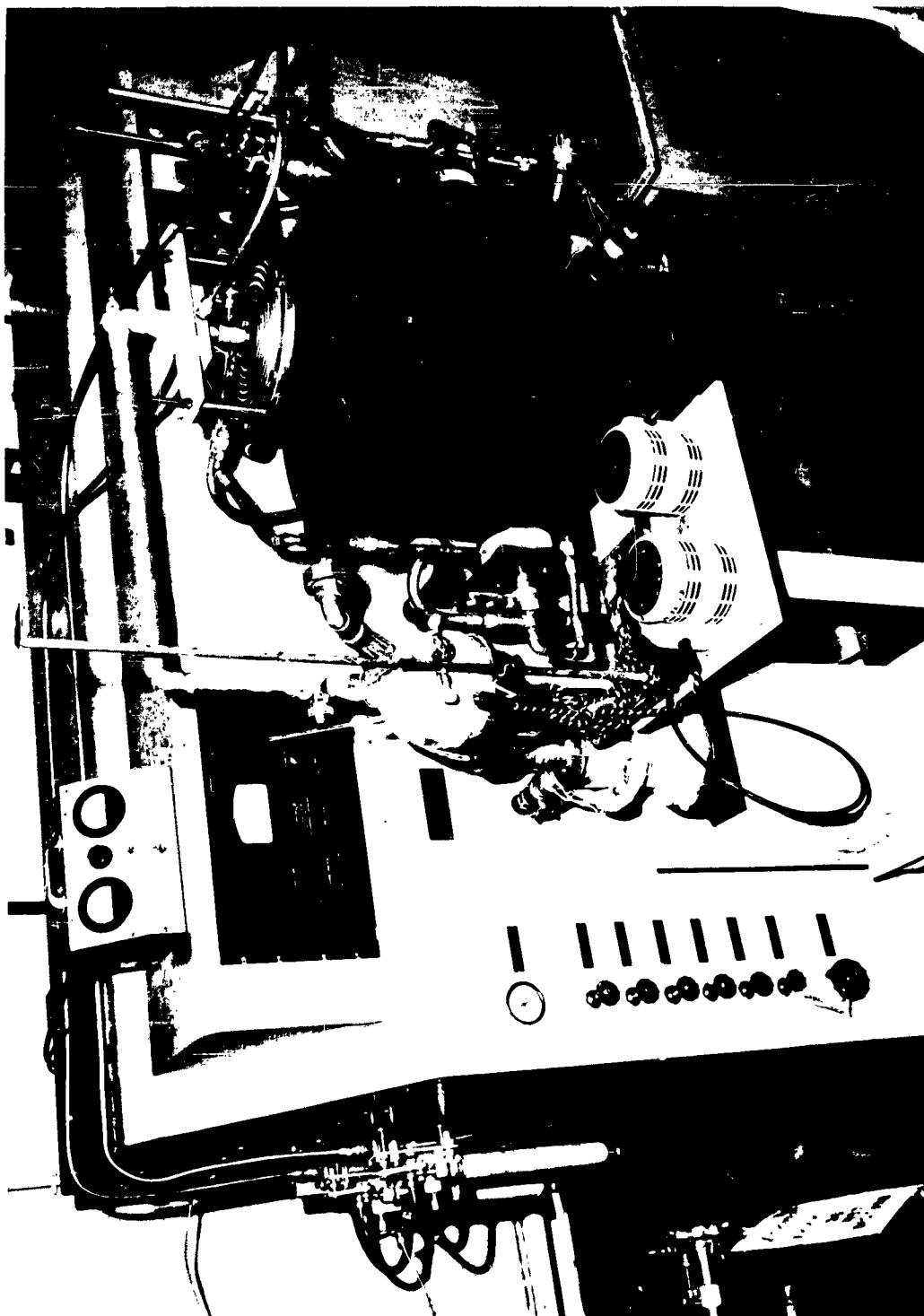
FIGURE 4   Vacuum Resistor Furnace Showing Cold Trap in Left Foreground

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FIGURE 5   Vacuum Resistor Furnace Showing Arrangement of Vapor Generators

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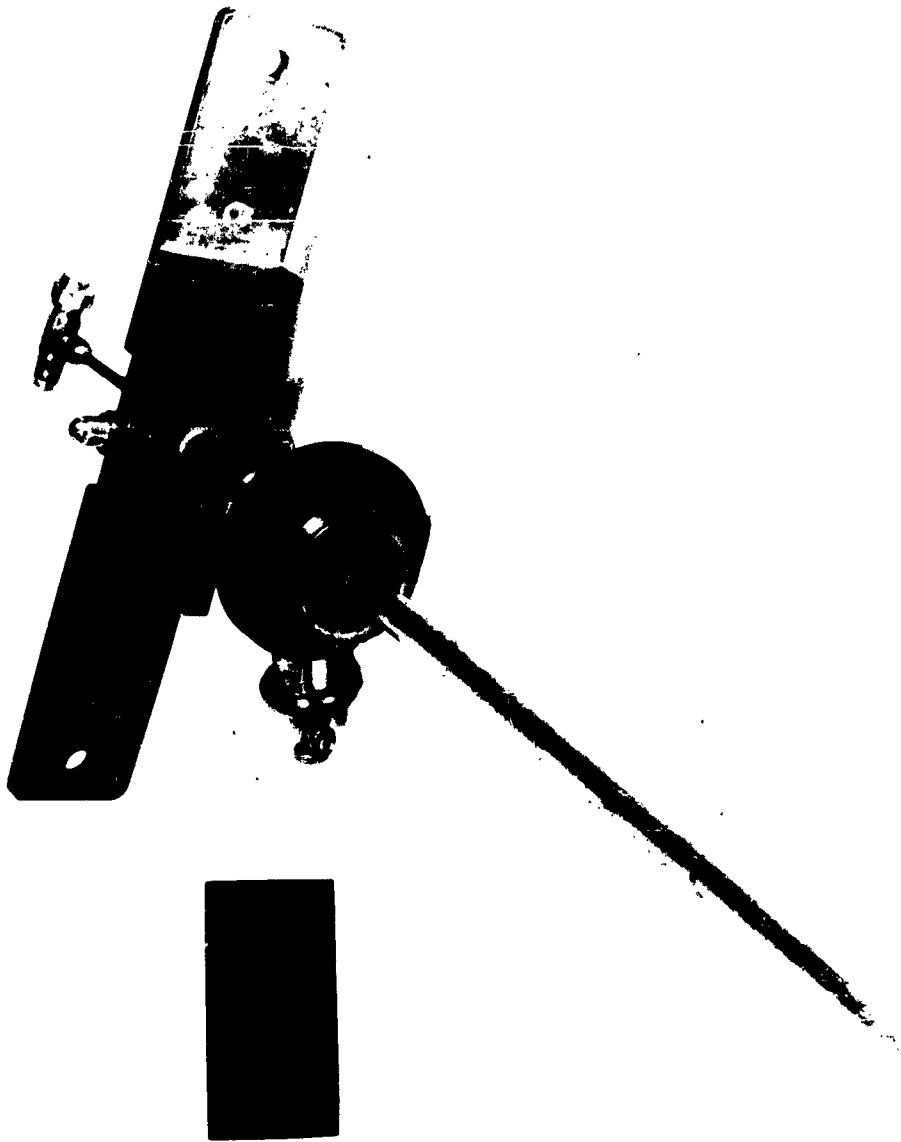
Gas Injector Design

FIGURE 6

IV. CHARACTERIZATION METHODS

The purpose of this program has been outlined as the development of new pyrolytic refractories with anisotropic properties by vapor deposition techniques. Preliminary experiments employing the glass vacuum system equipped with the induction furnace assembly served to screen and establish optimum conditions for the preparation of new pyrolytic materials. After determination of the influence of gas compositions, temperatures, flow rates, and substrate materials, large pyrolytic shapes have been prepared by use of the high-temperature graphite resistance furnace. In the area of synthesis, we have defined the scope of the program as establishing the following:

1. Optimum flow rate of source gases.

2. Optimum temperature of source gases.

3. Correct injector design.

    a. Proper injector to give uniform deposits.

    b. System geometry.

4. Optimum deposition temperatures.

5. Effects on the deposit of various substrates.

    a. AGSR and other commercial graphites.

    b. Pyrolytic graphite.

    c. Other materials.

6. Effects on the deposit of various substrate finishes.

7. Techniques for nondestructive separation of pyrolytic deposits from substrates.

    a. Machining.

    b. Chemical action.

    c. Substrate coatings.

Compounds of layered crystal structure are known to show markedly different physical properties in their basal planes and along their c-axes. As common examples, it is the ease with which shear occurs perpendicular to their c-axes which is basic to the use of graphite and boron nitride as lubricants, even though their hardnesses in the basal plane are great enough to warrant, in principle, their use as abrasives. This pronounced anisotropy extends to other properties of these compounds as well, as the crystallites of pyrolytically formed materials are more highly ordered, properties may be expected to be a function on their relative orientations. Though in most instances this expectation is undoubtedly confirmed, the influence of the intercrystal boundaries is always present and, in many cases, felt to be controlling.[23] For this reason a major portion of the property study program has been concerned with the determination of the relation of pyrolytic structure to variation of synthetic conditions.

Property studies were performed on samples obtained from successful depositions as follows:

1. Chemical Analysis - Compound stoichiometry, presence of reaction by-products, level of impurity, and reaction between the pyrolytic deposit and substrate materials were investigated by wet analysis and spectrographic techniques.

2. Infrared Absorption Spectra - Structural identifications were obtained where warranted with a Perkin-Elmer 221 recording spectrometer, fitted with a rock salt prism. Samples in paraffin oil, fluorocarbon mulls, or dispersed in potassium bromide pellets were investigated in the spectral region between 4000 cm^{-1} and 650 cm^{-1}.

3. X-Ray Diffraction Analysis - Microstructure, with respect to orientation, lattice parameters, and crystallite size by diffraction analyses were investigated on samples with copper Kα X-radiation in a Norelco X-ray spectrometer by standard techniques. Sodium chloride was used as an external standard to determine instrument line broadening and error. X-ray diffraction on powder samples enabled the determination of c/2 (the interlayer spacing), La (the effective crystallite dimension of the layers in the plane of the layer), and Lc (the dimension of the parallel layer group perpendicular to the layers). c/2 can be read directly from the diffraction pattern as it is simply the value of the 002 reflection. La is obtained from the peak breadth of hk reflections at half the maximum intensity.

$$La = 1.84 \ \lambda / B \ \cos \ \theta$$

where B is the half width of an hk reflection, and λ and θ have their usual significance. Likewise, Lc is obtained from the half peak breadth of the 002 or 004 reflection:

$$Lc = 0.89 \lambda / B \ \cos \ \theta$$

The 004 is preferable if the peak is strong enough to be well observed.

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A value for the preferred orientation may be obtained by measuring the integrated intensity of the 002 peak on a sample, as formed, perpendicular and parallel to the surface.

4. Microscopy - Aspects of microstructure were also observed by examination of polished cross-sections of samples embedded in Bakelite, by use of a Vickers projection microscope and the standard techniques of microscopy. Magnifications of 125X usually sufficed in polarized light.

Samples were examined with an RCA EMU2 Electron Microscope at magnifications of approximately 12,000X. Negative surface replicas were prepared with polyvinyl alcohol, preshadowed with chromium (angle ratio 3:1) and further replicas made by carbon coatings. Low power photographs of the same replicas at approximately 500X magnification can also be obtained.

5. Density - Density of small samples (ca. 0.25 mm^3) were determined by flotation in mixtures of tetrabromoethane and carbon tetrachloride, calibrated by means of standard pycnometry. Samples were titrated with the two liquids and the end-points could be read with sufficient sensitivity such that the principal error lies in variations within the sample.

6. Oxidation Resistance Study - No attempt as yet has been made to determine melting points, sublimation, or dissociation temperatures of the pyrolytic samples. However, a simple measure of oxidation resistance was obtained by observing changes in weight upon heating to 1500°C in laboratory atmosphere at varying lengths of time.

7. Hardness - Hardness measurements were performed by indentation measurements using the diamond indentor as an objective of the Vickers projection microscope.

8. Other Measurements - Other measurements, which the course of the investigation would indicate as desirable but which have not been performed, include: (a) tensile and elastic modulus and bend (traverse rupture), (b) soundness of specimens by ultrasonic and X-ray techniques, and (c) thermal conductivity.

V. RESULTS

In addition to establishing the conditions for preparation of new pyrolytic refractories, the relation of process variables to sample property has also been considered in order to determine optimum deposition conditions. Phase I of the program has been devoted to the development of background and technique in the field of vapor deposition. Partly because of the volume of research which has in recent years been published relating to pyrolytic graphite, the choice has been to investigate pyrolytic boron nitride, a structural analog in the nitrogen-boron system and an interesting material about which little is known. Phase II is concerned with the application of these techniques to the formation of coatings, large sound pyrolytic shapes, and the development of new materials.

In the program, the objectives of Phase I have been successfully completed. Synthetic conditions necessary to obtain high density, fine microstructure, and strength in the pyrolytic structures have been determined, and the synthesis of pyrolytic graphite and pyrolytic boron nitride is now sufficiently well understood such that several large samples have been prepared. Application of the principles derived has shown their soundness and resulted in a few new pyrolytic alloys.

A. PYROLYTIC BORON NITRIDE

The pyrolysis of the vapor of any simple compound containing boron-nitrogen bonding would undoubtedly result in pyrolytic boron nitride. The original intention here was to employ mole per mole mixtures of boron trichloride and ammonia, but because of the advantages offered by use of a single compound such as borazole, this was immediately abandoned. There proved, however, to be no commercial source of this compound. However, one vendor did quote a completely prohibitive price for a custom synthesis. Further, borazole was found to suffer from the disadvantage of instability towards polymerization when stored at room temperatures. About one year ago U. S. Borax and Chemical Corporation announced the availability of B-trichloroborazole, $B_3N_3H_3Cl_3$, and inquiry revealed an attractive price, stability, and desirable physical properties. Its choice has proved to be a satisfactory one.

In the early screening runs, consideration was given to the advisability of transporting the source material to the heated substrate by use of a carrier gas. To this end, experiments were performed in which a nitrogen sweep was employed but resulted in no deposits being obtained. The choice of nitrogen may have been ill-advised. For example, use of argon as a carrier

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for nickel carbonyl allows one to obtain a nickel deposit at 60°C, while the use of carbon monoxide, which supresses the carbonyl dissociation, gives a nickel deposit only above 150°C. Although the mechanism of the pyrolysis reaction of B-trichloroborazole to yield boron nitride is not well understood, possibly nitrogen may behave in a fashion similar to carbon monoxide. In any event, an attempt using an argon carrier gave only very slow deposition, and in view of the success achieved in the system under reduced pressure, this approach was not considered further.

Depositions occurred with relative ease provided a scrupulously air-tight vacuum system was maintained. Figure 7 is representative of the samples prepared. They are generally hard, light in color, sound, and non-porous. Analytical data proved that very pure boron nitride was obtained, boron to nitrogen ratios of 0.99/1.00 being usually found, while spectrographic analyses showed heavy metals to be present only to the extent of less than 0.1%. Undoubtedly prepurification of the starting material would reduce them further. Infrared analysis of several samples further substantiated the absence of reaction by-products and gave excellent comparisons with reported spectra,[32,33] with broad absorption at 7.25 and 12.25 microns, and with little else being found.

During the course of sample preparation the causes of the various colorations observed in the boron nitride products became a matter of concern. Although the samples appeared to be comparable in all other respects, the exact conditions which gave a sample color--for example, ivory white in one case in preference to a yellow-brown in another--were not clear. It soon became possible to discard an early thought that this was an effect of deposition rate that gave varying densities, orientations, crystallite sizes, etc., in the product. Color variations were found to be caused by only very slight amounts of product impurity from stopcock grease, Pyseal wax, or minute quantities of decomposition products remaining from previous runs. It was also shown that care must be taken to provide pure samples for the characterization studies in order to obtain meaningful and reproducible results. For example, a very light yellow sample and a black sample of boron nitride prepared under identical experimental conditions were found to differ in density by 0.5 g/cc.

In order to optimize the conditions of the deposition process, runs were performed under a variety of screening conditions in the glass systems. Principally samples obtained at deposition temperatures of 1300°C, 1500°C, and 1700°C and at flow rates provided by B-trichloroborazole source temperatures at 25°C, 45°C, and 60°C (0.1 mm, 1 mm, 5 mm vapor pressures) and some intermediate values were sufficient to obtain data relating microstructure, deposition rates, density, crystallite size, etc While it soon became obvious that a completely systematic study was beyond the scope of the program, some interesting results were obtained and are summarized here.
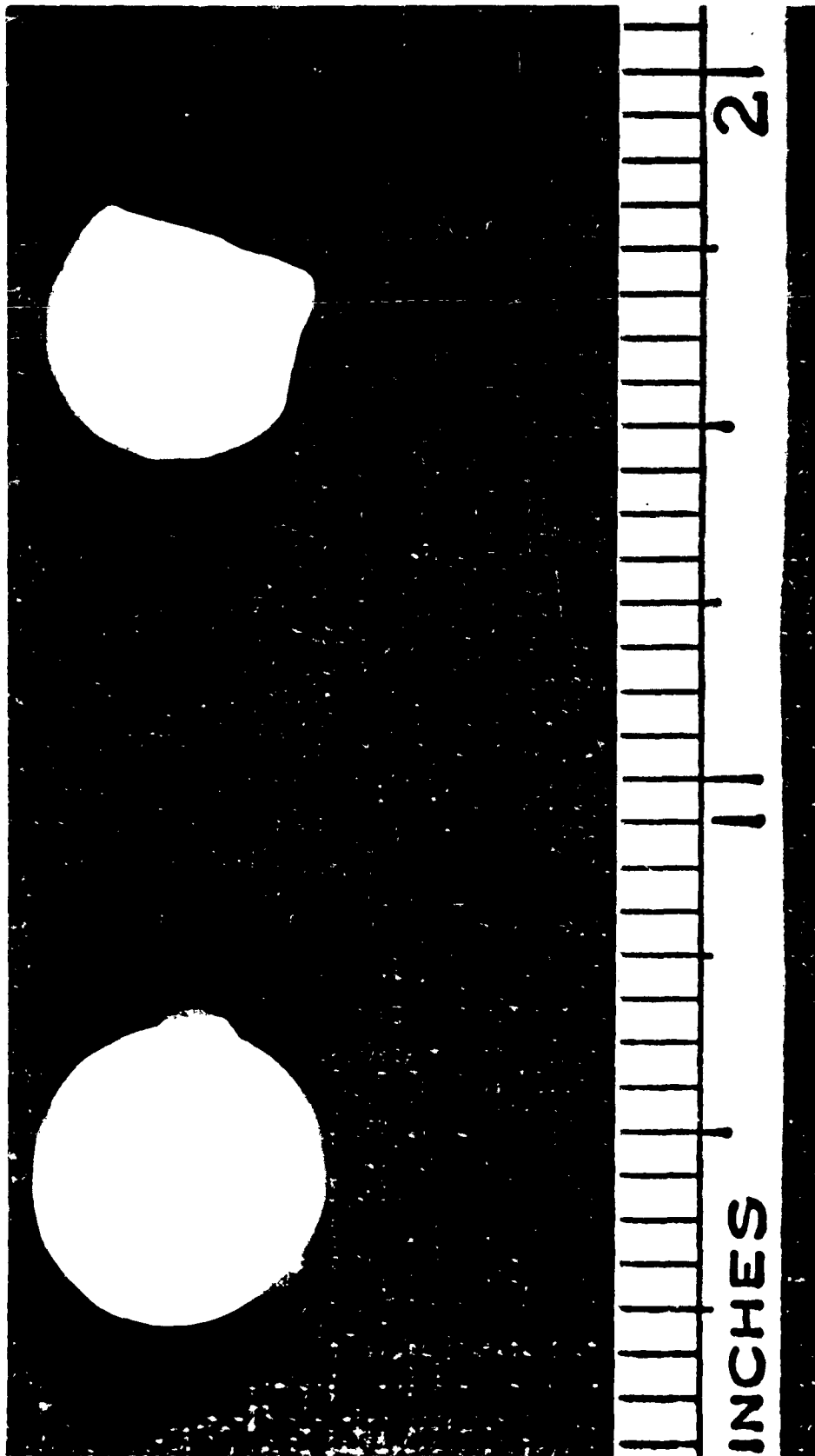
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FIGURE 7   Pyrolytic Boron Nitride Samples Deposited on AGSR Graphite Susceptor

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Rates of deposition were found to be strongly influenced by the rate at which gas molecules reach the substrate. At very low source material vapor pressure, the rate is approximately constant with deposition temperature and, for a pressure of approximately 0.1 mm of B-trichloroborazole, is roughly 1 mil per hour. It has been observed, repeatedly, at this flow rate that no deposit is obtained at temperatures in excess of 1700°C, but as these experimental conditions are of little interest, the point was not pursued further.

At a vapor generator temperature of 45°C, the rate is constant at approximately 5 mils per hour to 1500°C, but above this value, becomes very temperature dependent, rising to 12-15 mils per hours at 1700°C. At 60°C vapor generator temperature, the rate is constant at 10 mils per hour at 1500°C, but rises sharply to a value of 30-40 mils per hour at 1700°C. Deposition rates of 100-150 mils per hour are easily obtainable at slightly higher B-trichloroborazole source temperatures.

Density values are also highly dependent on deposition temperatures and gas flow rate, as summarized in Figure 8. These curves are a result of a large number of runs and are believed to be generally accurate although some deviations were observed. The density of boron nitride is reported to be 2.20 g/cc.[34] The maximum value attained in this work is 2.14 g/cc with values above 2.00 being usually observed. Thus porosity is quite low. Higher densities were achieved at slower deposition rates and rose rapidly at 1500°C to approach theoretical density asymptotically in a manner analogous to that of pyrolytic graphite although at much lower deposition temperatures.

Hardness values were found to be very difficult to obtain reproducibly by the indentation method and none will be reported. Both the difficulty in observing the sample surface because of the high degree of light reflection and the elasticity of the material made the values unrealistic.

The results indicated that pyrolytic boron nitride undergoes appreciable erosion only above 1200°C in strongly oxidizing atmospheres with no discernible dependence on any process variable. In all cases a protective, glossy oxide is formed on the boron nitride when heated to 800-1000°C. At 1200°C a slow, continuous oxidation occurred, and at 1400°C the rate was more rapid. At the higher temperatures (1400°C and above) the high volatility of boron oxides and nitrogen caused a rapid loss of material.

Considerable work has been done in determining the microstructure of the pyrolytic boron nitride deposit. In polished cross sections, the deposit displayed the well-known cone-shaped columnar structure that is characteristic of pyrolytic graphite,[1, 35] with the tips of the cones originating at or near the graphite substrate (Figure 9). The extensive horizontal cracking present is caused by improper cooling from reaction temperature or by the cutting procedure.

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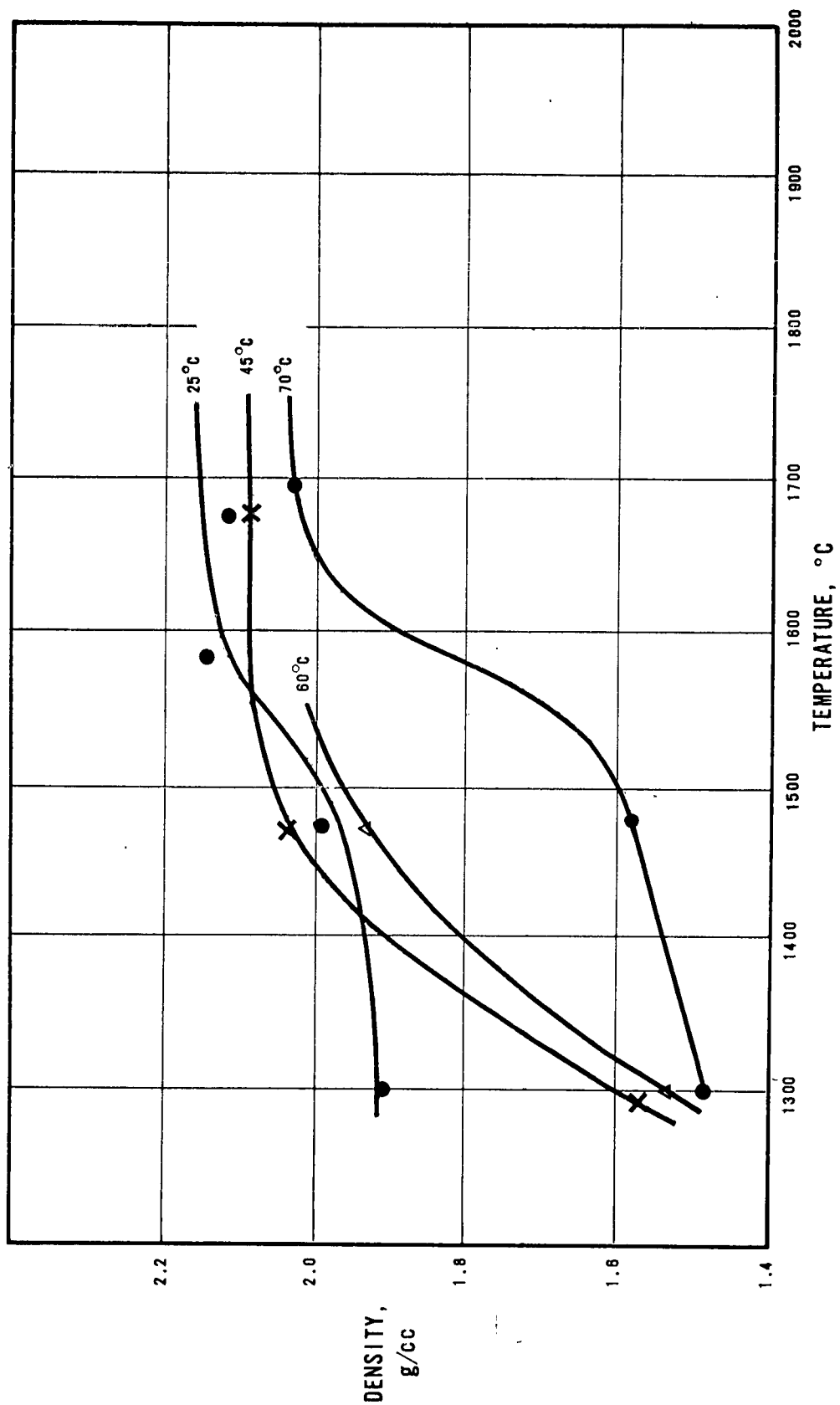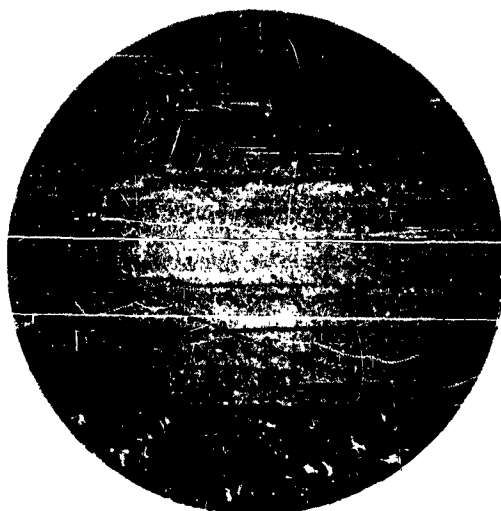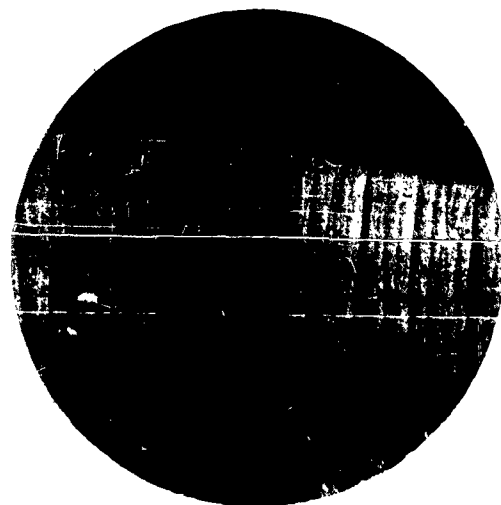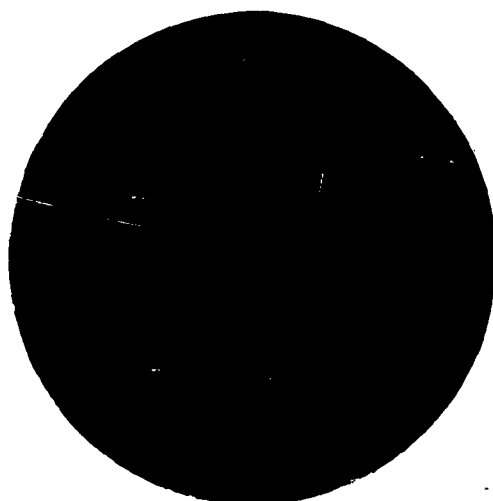FIGURE 8   Densities of Pyrolytic Boron Nitride Prepared at Various Temperatures and Source Vapor Pressures

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FIGURE 9   Cross-Section Photomicrograph of Pyrolytic Boron Nitride
            Prepared at 1700°C at 4 Separate Source Material Flow Rates.
            (B-Trichloroborazole Source Material Temperature at (a) 25°C,
   (b) 45°C, (c) 60°C, and (d) 75°C, Magnification 72X)

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It is generally accepted that a long, very narrow, or continuously regenerated cone structure is representative of a less stressed condition and structural strength within the deposit. Therefore, no other single aspect of this work is more critical to the eventual service of these materials than the relations between microstructure and process variables. It was established that cone structure is essentially independent of deposition temperature and that source material flow rate is probably the most important single variable. The samples shown were prepared at 1700°C. At a source material temperature of 25°C (B-trichloroborazole vapor pressure = 0.1 mm), the deposit was essentially without this microstructure, and only rarely can the presence of any type of cone structure be discerned. Source material temperatures of 60°C (4 mm) gave very large and randomly ordered cone structures while at 75°C (8.5 mm), the samples were very brittle with extensive cracking occurring along the cone boundaries and horizontally in a scalloped pattern. The preferred structure was obtained at a moderate B-trichloroborazole flow rate provided by maintaining the source at 45°C (vapor pressure = 1 mm). The results were accurately reproducible to within 5° vapor generator temperature.

Some consideration was also given to the effect of susceptor materials upon the pyrolytic deposit. Hot-pressed boron nitride was believed to have considerable merit as a material upon which to deposit pyrolytic boron nitride. Consequently, the feasibility of heating hot-pressed boron nitride inductively at very high frequencies was investigated. An induction heater operating at 120 megacycles and rated at 1.25 kilowatts employing a five-turn primary water-cooled copper coil was used. At full output of the power generator, a rise in temperature of only 300°C was attained; this indicated that boron nitride would be of little or no use as a susceptor at this point in the investigation.

Tungsten susceptors were employed, but adherence of the deposit was greatly inferior compared to the graphite substrates. Photomicrographs of cross sections showed the cone structure, although somewhat less well defined, and X-ray fluorescence and diffraction analyses gave no indication of the formation of tungsten boride or nitride in the bulk of the deposit.

Polishing the AGSR graphite susceptor resulted in no discernible effect on the deposit. The result of using Raytheon Company's pyrolytic graphite is shown in Figure 10, the upper photograph being a view of the top surface of the susceptor.

Here the boron nitride is deposited in the direction of the cone structure of the susceptor and assumes some of its features, whereas the lower photomicrograph is a view of the side where a random cone structure has grown perpendicular to that of the pyrolytic graphite.
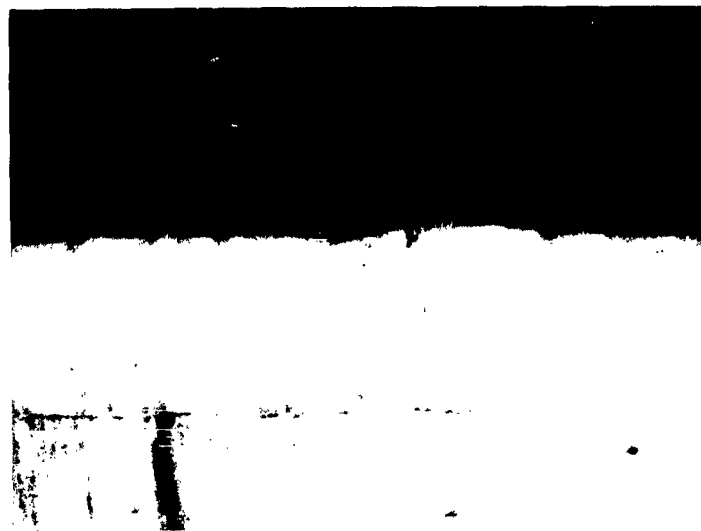
COATING

SUBSTRATE

SUBSTRATE   COATING

FIGURE 10   Cross-Section Photomicrographs of Pyrolytic Boron
Nitride Deposited on Top Surface (upper) and Edge
(lower) of Pyrolytic Graphite Susceptor
(Magnification 240X)

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The structure of pyrolytic boron nitride can best be understood in terms of the structure of boron nitride. In the well-ordered material, the layers are superposed with nitrogen and boron directly above one another.[36] Thus, this differs from graphite where in every second layer there is an atom directly above the center of a·hexagon of the layer below. However, the similarities in the two structures are striking with the interlayer separation in boron nitride being 3.33 Å, compared to 3.35 Å for graphite; further, the layer sequence is ABA in both materials, although, as seen above, for different reasons.

The X-ray pattern of boron nitride, according to the AST Hamawalt file is shown in Table IV.

TABLE IV

X-RAY PATTERN OF BORON NITRIDE

d (Å)	I/I_1	hkℓ
3.33	100	002
2.17	15	100
2.06	6	101
1.817	13	102
1.667	6	004
1.552	1	103
1.332	3	104
1.253	6	110

In pyrolytic materials the layers are deposited in parallel sheets but have no three-dimensional order, much like a randomly dropped pack of cards. Because of this three-dimensional disorder, there are no three-dimensional reflections. Instead the (00ℓ) reflections measure the interlayer spacings directly, and the (h, k) reflections with their highly asymmetric shape replace the three-dimensional reflections in ordered material.

X-ray studies have confirmed that pyrolytic boron nitride does have a layer structure analogous to that of pyrolytic graphite[1] with the shape of the (h, k) peak being well defined (Figure 11). The (00ℓ) reflections are invariably
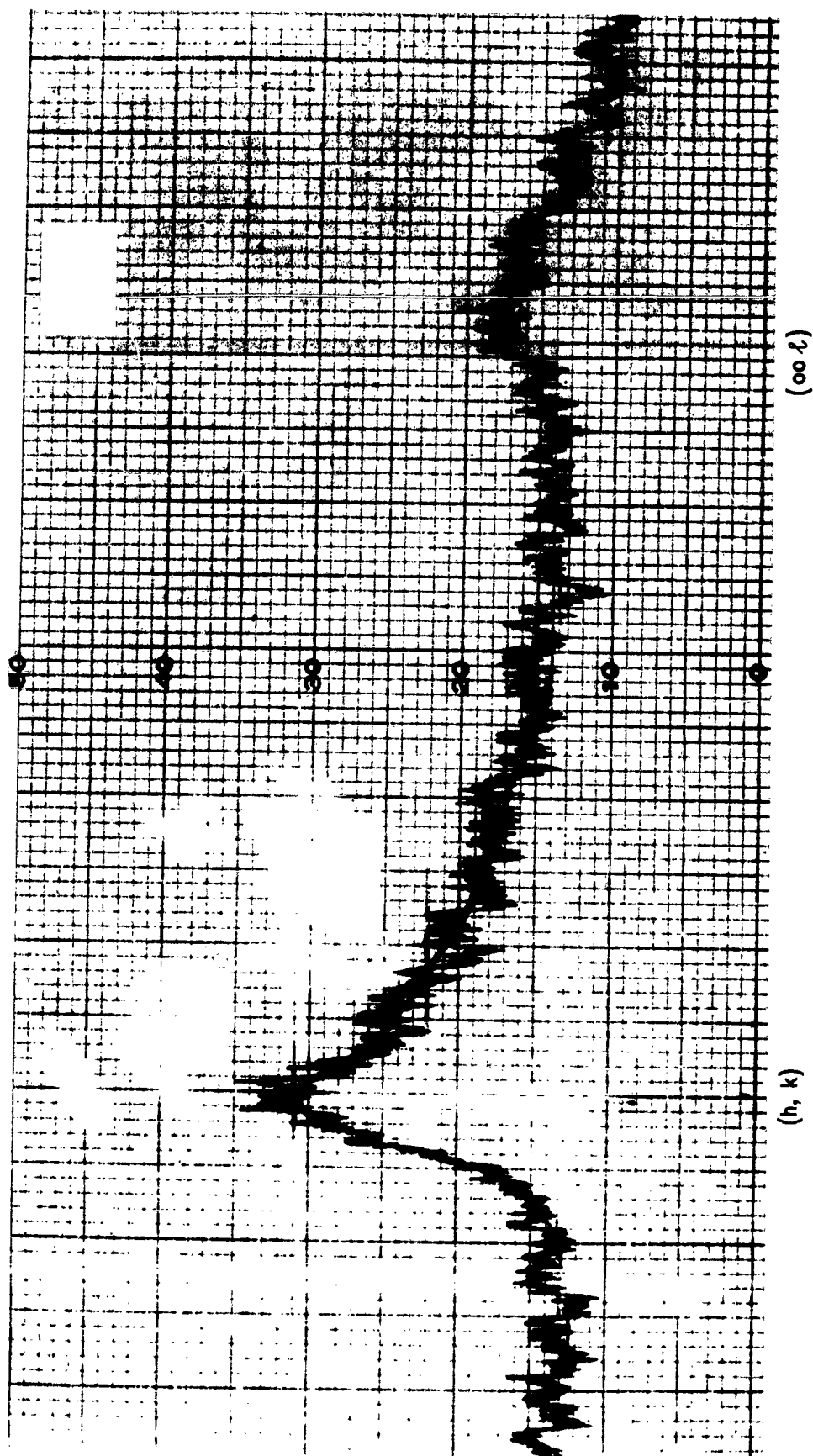
36

FIGURE 11   The Asymetric (h, k) Reflection of the Pyrolytic Boron Nitride X-ray Powder Pattern

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broad and displaced to higher ℓ values corresponding to interlayer c/2 spacing values in the range of 3.45 to 3.47 Å. High values are also observed with pyroltic graphite as will be seen and are taken as typical of the structure. Crystallite sizes vary irregularly with the deposition conditions although values of L_a and L_c' usually result in the 50 to 100 Å range. Though no completely unambiguous relationship could be drawn between the process variables and the X-ray data, low source material flow rates were found to promote larger crystallite size and small interplanar distance within the pyrolytic sample. However, from the values obtained, decreases in interplanar distance are often insufficient to account for the density increases observed, and the relationships between these properties and cone structure were not completely apparent.

Small cylinders of pyrolytic boron nitride will be cut ultrasonically from which a measure of preferred orientation will be obtained.

B. PYROLYTIC GRAPHITE

A similar but more limited program was undertaken to determine the feasibility of preparing pyrolytic graphite from benzene. This represents a departure from the sources used by other investigators who generally have chosen methane or other open-chain hydrocarbons.[1,23,38] The ease of handling and the structural similarity to graphite rendered it attractive. Depositions were performed at benzene source temperatures from -35°C to -10°C (1 mm to 10 mm vapor pressure) at substrate temperatures of 1300°C to 2100°C.

The results appear to substantiate those of other workers in the field with two possible exceptions. First, the pyrolytic graphite prepared from benzene had a silver-gray, metallic luster and appeared to be of higher hardness than other samples we have observed. Second, we have been unable to reproduce an experiment performed at the Bell Telephone Laboratories.

They report, "....pyrolytic carbon is graphtic in nature and thus can be considered as originating from aromatic hydrocarbons which possess similar hexagonal ring structures. Isolation of benzene, naphthalene, anthracene, and more complex aromatic compounds from the pyrolysis of methane is evidence that the aromatization of methane is probably an intermediate step in the formation of the pyrolytic graphite. It is therefore to be expected that the use of benzene should increase the rate of carbon deposition, and this increase is observed. Similarly, the use of toluene or xylene, leading to the formation of aromatic radicals, should, as is observed, provide even more rapid deposition than does the use of benzene."[23]

To investigate this observation, several runs were made under the conditions where benzene gave pyrolytic graphite but where toluene was sub-

stituted as the starting material. In each of the runs performed, only very slow deposition was obtained. Experiments have also indicated, in agreement with the results of Brown and Watt,[39] that propane is the most suitable hydro-carbon for high deposition rate.

Runs were performed without regard to systemization, and a scatter of data was collected. No carrier gas was employed to transport the benzene to the susceptors.

Photomicrographs revealed the characteristic cone microstructure, of which Figure 12 is representative. Large primary cone structures were generally observed with very fine secondary structure imposed upon them. As in the case of pyrolytic boron nitride, X-ray data revealed $c/2$ interlayer spacing of 3.45 Å to 3.50 Å (graphite = 3.35 Å) and crystallite dimensions L_a and L_c between 50 Å and 150 Å. Density values less than 2.00 g/cc occurred only infrequently (graphite = 2.26 g/cc) although values approaching theoretical require much higher pyrolysis temperatures than in boron nitride depositions. Alteration of process variables also has essentially the same effect on the microstructure.

C. DEVELOPMENT OF LARGE PYROLYTIC SHAPES

Early in the program efforts were directed to the application of the principles derived from the screening runs to the formation of large pyrolytic samples and rocket-nozzle test pieces for property evaluation. In order to study the parameters for successful deposition of coatings and sound pyrolytic shapes in the graphite resistance furnace, thirty-four 30-hour, and several shorter deposition runs, have been carried out.

Final testing of the furnace and accessories consisted of two runs in which pyrolytic graphite and pyrolytic boron nitride were deposited onto AGSR graphite rods, the ends of which were machined into the shape of a truncated hemisphere to determine whether preferential deposition would occur on one particular surface. No difficulty was encountered in maintaining the furnace at 2100°C or keeping the injector cool, which was within 1-1/2 inches of the substrate; deposition occurred evenly on all surfaces of the substrate, although in both cases only the upper half received any appreciable deposit.

In the pyrolytic boron nitride run, the B-trichloroborazole assembly was maintained at 45°C corresponding to a B-trichloroborazole vapor pressure of 1 mm. The water circulating system of the injector was found to operate with such efficiency that warm water had to be introduced to maintain it at 55°C. In a 12-hour run the result was a very smooth, hard, and even layer of yellow product in the flat top and hemispherical surface of the substrate, while extending

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COATING

SUBSTRATE

FIGURE 12   Cross-Section Photomicrograph of
Pyrolytic Graphite Deposited on AGSR
Graphite Susceptor
(Magnification 120X)

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1-1/2 inches further down on its sides was a zone covered with a thin, nonadhering, light-gray powder. The remainder of the surface was unaltered. Both yellow and gray samples resembled pyrolytic boron nitride obtained in the past and proved to be such. Although there was no evidence of boron carbide formation, a 1% carbon impurity was found in the samples. The impurity was subsequently eliminated only by prolonged "baking out" of the furnace packing.

With pyrolytic graphite, deposition again occurred equally on all surfaces of the substrate. A 4-hour run with the benzene maintained at approximately -20°C (vapor pressure = 5 mm) resulted in a maximum thickness of 5 mils. Thus the yield was quite low, and the advisability of depositing into AGSR graphite cavity substrates was then considered.

With this objective pyrolytic hemispheres were prepared by deposition into molds machined into graphite blocks (Figure 13). In a typical experiment a pyrolytic boron nitride hemisphere 2-1/2 inches in diameter and 275 mils thick at its apex tapering to 100 mils thickness around its skirt was prepared and is shown in Figure 14. The furnace temperature was 1800°C, and the source material was held at 75°C.

The deposit obtained was very hard, nonporous, and relatively evenly coated in the mold though increasing uniformly in thickness from edge to apex. However, as shown in the illustration, upon standing for several weeks, the deposit began to develop appreciable cracking, consistent with the rapid deposition rate and due to the stresses imposed by the differences in thermal expansion coefficients between the deposit and the heavy graphite mold.

Most forms of deposition result in some internal stress being incorporated into the deposit. That stresses are also induced between the graphite substrate and the pyrolytic boron nitride upon cooling from reaction temperature was demonstrated by two experiments performed in preparing pyrolytic rings, illustrated in Figure 15. The ring on the right has had the graphite base removed, and the deposit is shown to have sprung back to a stress-free, closed position while the one on the left is as taken from the furnace.

In the preparation of uncracked hemispherical shapes, the influence of the graphite substrate was greatly diminished by plating into hemispherical shells (Figure 13), and depositions of pyrolytic boron nitride were made at B-trichloroborazole source material temperatures of 55-60°C representing a compromise between acceptable microstructure and deposition rate. No boron nitride hemisphere prepared under these conditions has cracked. No special precaution was found necessary in depositing pyrolytic graphite. Some samples are now six months old and still sound, as shown in Figures 16 and 17.

41
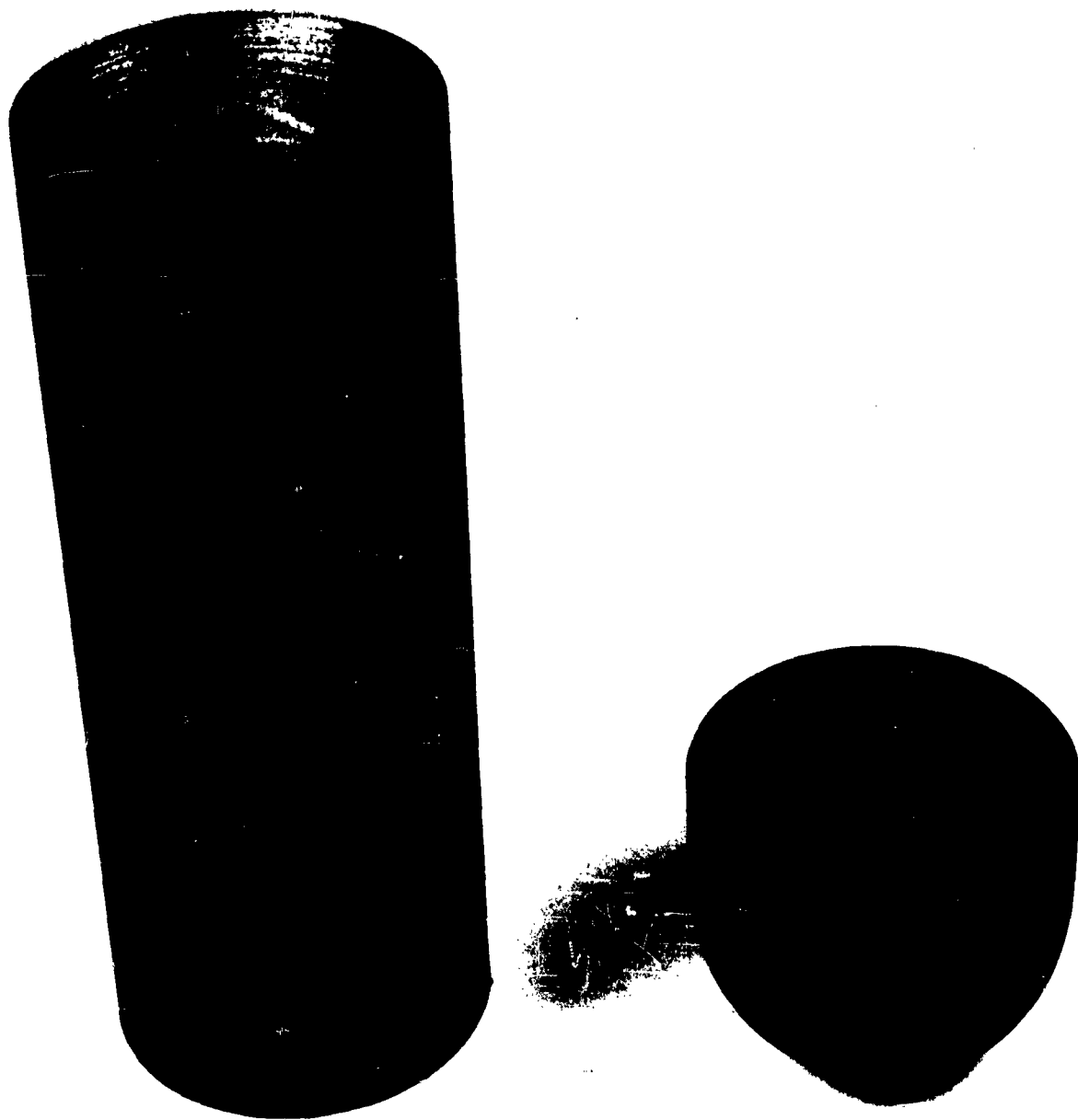
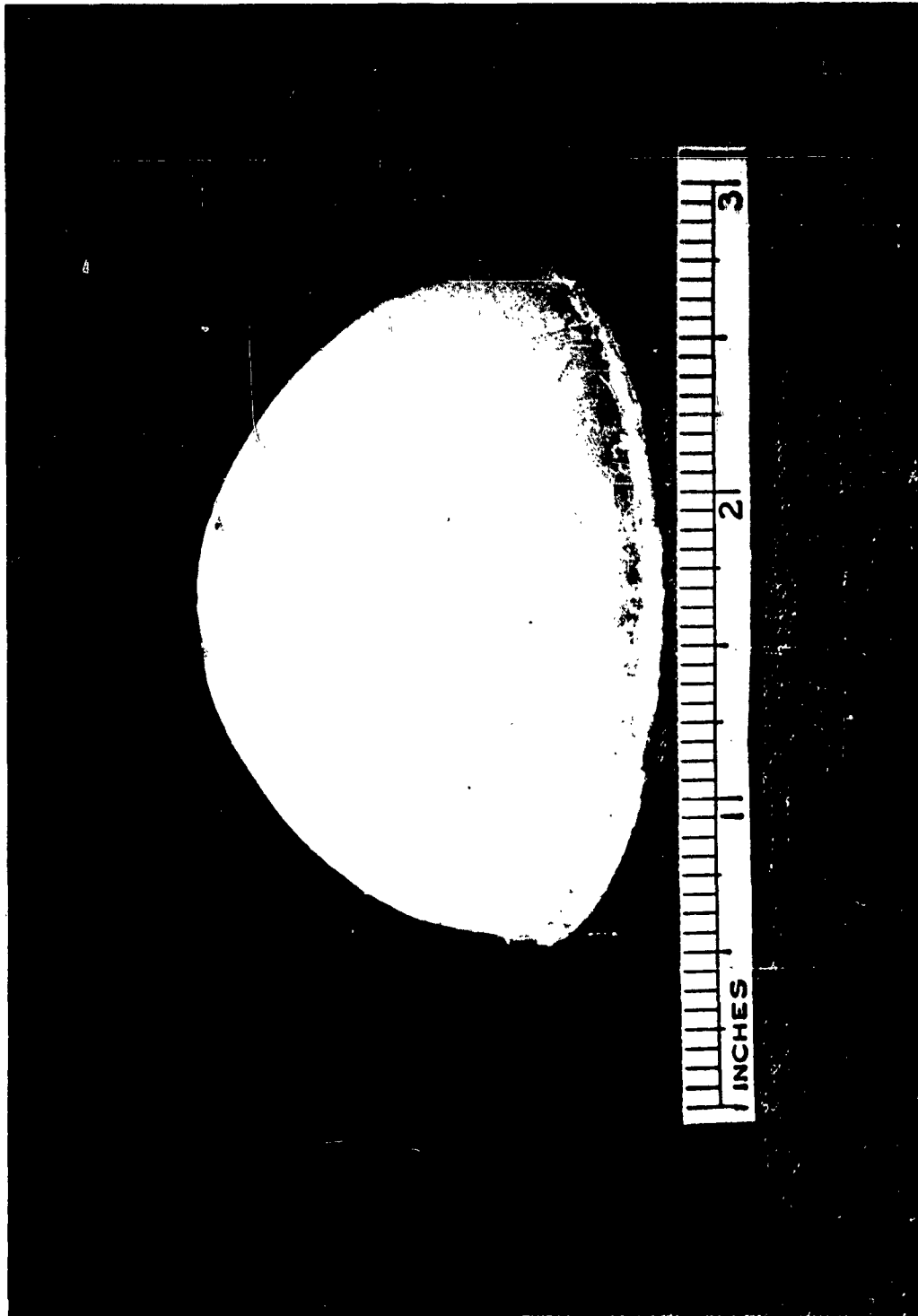FIGURE 13   Cavity Substrates for Deposition of Pyrolytic Hemispheres

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FIGURE 14   Cracked Hemisphere of Pyrolytic Boron Nitride

FIGURE 15 Pyrolytic Boron Nitride Ring Before Removal of Graphite Substrate (left) and After Removal of Substrate (right)
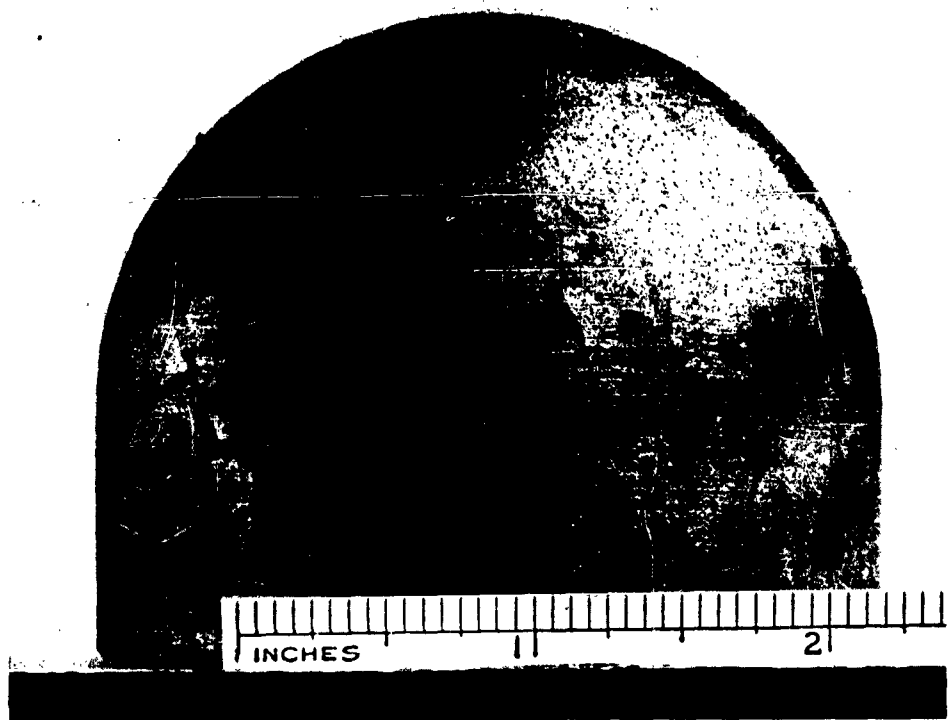
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FIGURE 16   Uncracked Hemisphere of Pyrolytic Graphite (unpolished)
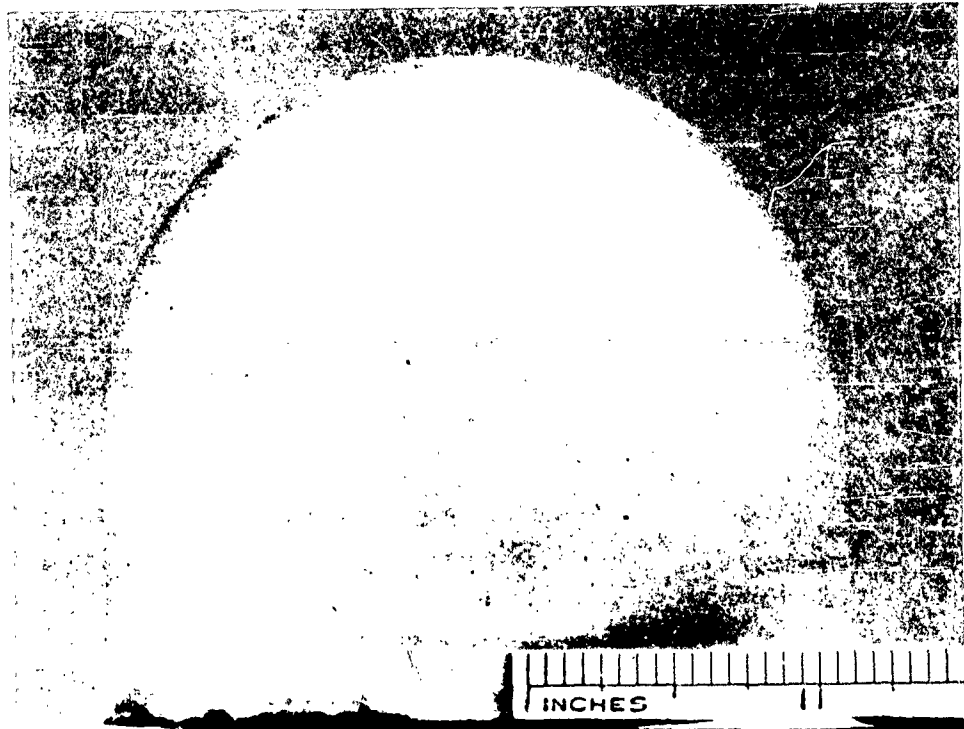
FIGURE 17   Uncracked Hemisphere of Pyrolytic Boron Nitride

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A major consideration also had to be given to the best method of nondestructive separation of the pyrolytic deposits from their AGSR substrates. Several heat-resistant materials, available from the Minnesota Mining and Manufacturing Company as mold coatings, as well as the use of frangible mandrels and delaminating materials, were investigated to little avail. Machining the substrates from the deposits was considered to be of some merit, though probably not suitable for anything but the simplest shapes.

A very satisfactory method however has been developed whereby the separation is achieved by chemical means. The ability of graphite to form compounds by inclusion of foreign substances within its structure has been known for many years, and compounds so formed have been examined in considerable detail.[39]

Graphite will react with mixtures of concentrated sulfuric and nitric acid to form interstitial compounds in which the graphite lattice expands to incorporate the anions HSO_4^- and NO_3^- together with molecules of acid, causing the graphite to swell (the interplanar distance in these compounds is about 8 Å; graphite = 3.35 Å) and flake away. This reaction occurs very rapidly but may be facilitated by washing off freshly formed layers, as the "graphite salts" are instantly decomposed by water. Graphite shows a remarkable specificity in this reaction. Other solutions such as sodium chromate-phosphoric acid were much inferior to the oxidizing conditions given by H_2SO_4-HNO_3 while concentrated sulfuric acid or nitric acid individually did not react in this manner at all.

Pyrolytic graphite and boron nitride were unaffected by the acid mix, even after standing for several hours, and although originally there was concern that serious attack might especially occur in any minute cracks in the pyrolytic deposit, in reality no reaction occurred.

The preparation of flats was found to be considerably more difficult than the preparation of other pyrolytic shapes, and investigation of suitable plating geometries in order to eliminate severe cracking and warping owing to nonuniform deposition and search for substrate materials compatible with the deposit led to a consideration of a number of novel substrate designs.

In order to obtain more satisfactory matching of thermal expansion coefficients, attempts were made to accomplish deposition onto pieces of pyrolytic boron nitride prepared in previous runs, which, because of minute cracks or insufficient thickness, were not generally satisfactory. Runs were made as previously, but particularly poor deposits were obtained being very thin, blistered, severely cracked, and usually carrying the imperfections of the substrate. The use of flat shapes of hot-pressed boron nitride gave virtually an identical type of deposit.

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As a one-shot experiment, the feasibility of using a fluid substrate such as provided by a thick layer of boron nitride powder in elimination of stresses induced by heavy graphite bases was considered. Here, the quality of the deposit was also poor, and resembled a very random pile of misshapen buckshot, with a deposit 1-inch thick at one point, 100 mils at another, and intermediate values elsewhere with many spots receiving no coating at all.

The experiments served well to illustrate the important relations that exist between the quality of the deposit and the nature of the nucleating surface on which it has been formed. Investigation of a number of graphite grades showed that from the point of view of surface quality, grain structure, and the thermal expansion matching with the pyrolytic deposit, National Carbon Company's ATJ grade was most suitable and was employed as substrate material for the remainder of the program.

The simplest plating geometry is provided by deposition normal to a flat surface. In one set of experiments deposition was made onto graphite flats 3-1/2 inches in diameter, the limitation imposed by the furnace cavity.

Although, as may be expected in this design, the deposit decreases from a maximum thickness at the center of the disc toward the periphery, this is usually a satisfactory approach. Since the plating efficiency of this substrate was low, an improved design was employed. It consisted of a cavity cut into a graphite rod to a depth of 2 inches, leaving very thin walls. A disc formed in the base of the cavity is shown in the lower right corner of Figure 18.

There appear to be no data available, but our experience indicates that the coefficient of contraction of ATJ graphite is much greater than that of the pyrolytic materials. The sample in the upper portion of Figure 18, which is shown to be bowed and cracked away from the substrate, is one indication of this conclusion. The disc formed in the cavity was also of insufficient thickness to withstand the compression imposed by the walls of the substrate and was severely cracked. Thus, as in the case of the hemispheres, it is desirable to make substrates of very thin graphite and to form deposits in substantial thicknesses, although due consideration must then be given to the problem of warping.

As a large portion of the deposition occurred at the walls of the cylindrical cavity, the next experiments were performed in box cavities cut into graphite blocks to utilize the flat sides. Invariably, however, unacceptable deposits were obtained as the corners of the boxes were not coated, and the nonuniformity of the deposit again resulted in cracking. The bottom of the box did not plate well, and regardless of the injector's position, 80% of the deposition occurred on the walls in a ring within 1-inch depth from the injector.

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FIGURE 18   Common Causes of Failure in the Preparation of Pyrolytic Flats

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This design obviously gives very poor gas flow properties and was abandoned. It was then hoped that pumping the vapors down a square graphite pipe open at both ends would result in improved gas flows and be more acceptable for obtaining uniform coating over a larger area. This proved not to be the case, however, and the result was exactly as with the box substrate in the one experiment attempted.

Noting the success encountered in preparation of the hemispheres, substrates were fashioned in the shape of a shell box with hemispherical bottom (or a hemisphere having four square sides). This hemispherical bottom is considered important in producing a smooth gas flow along the inner walls. Although this is not a simple die to form in a thin shell, some excellent deposits which were smooth, uncracked, and relatively uniform were obtained. However, in attempts to achieve deposit thicknesses greater than 25-50 mils, results were unfavorable owing to preferential deposition at the centers of the box faces, away from the corners, and because of extensive cracking owing to deposit nonuniformity (Figure 19).

For the preparation of pyrolytic flats, this cursory investigation of a number of substrate designs appears to offer little advantage over the use of a flat disc. In addition to proper matching of coefficients of thermal expansion, uniform deposit thickness over a large area and c~nical homogeneity will promote crack-free samples.

There is one further aspect of pyrolytic deposition which needs to be considered. In the present work with boron nitride and that of others,[40] it has been a common observation that the pyrolysis of boron trichloride and ammonia or its equivalents produces large volumes of very flocculent boron nitride powder (probably corresponding to soot in the carbon system) which may also contain significant levels of by-products. Aggregates of this boron nitride dust may be a cause of the cone microstructure, forming large nuclei on which atom-by-atom deposition proceeds. Not only does this material precipitate onto and block the injector--the sample on the lower left in Figure 18 is one formed where the diameter of the inlet gas stream was progressively diminished by this action; the piece is over 1-inch thick in the center--but also of more pressing concern is the observation that pockets of this low density material have been found in the pyrolytic deposit, particularly in the centers of large cones. Obviously, it is very desirable to limit the formation of this material to exclude it from the deposits, and moderate deposition rates have eliminated it entirely.

In this manner, the discs of pyrolytic graphite 100 mils thick and 3 inches in diameter and pyrolytic boron nitride 170 mils thick and 2-1/2 inches in diameter, as shown in Figures 20 and 21, have been prepared.
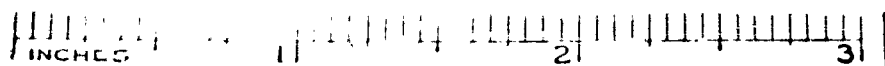
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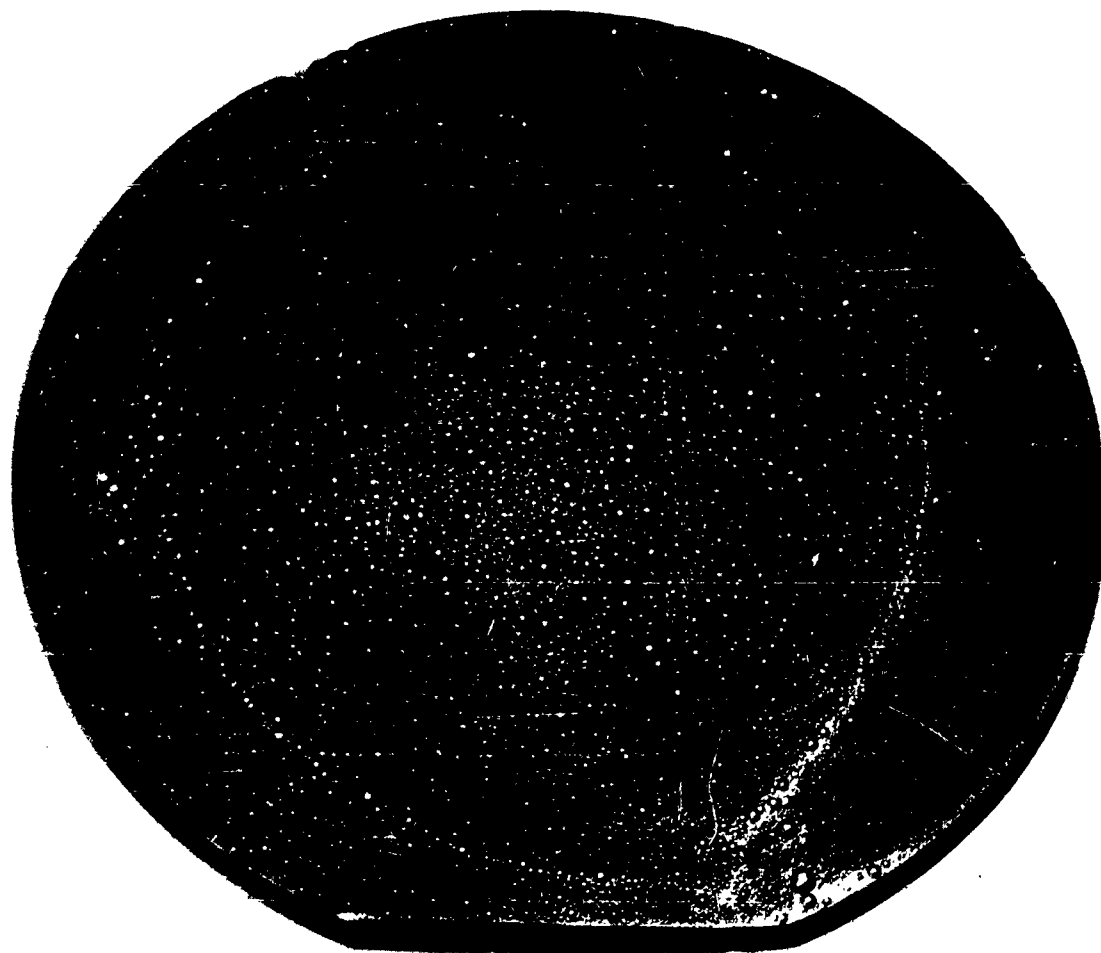FIGURE 19   Deposition Into a Box Substrate

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FIGURE 20   Pyrolytic Graphite Disc

FIGURE 21   Pyrolytic Boron Nitride Disc

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In conclusion of this discussion of these two materials, one principal comparison should be stated which has been described only by implication in the preceding sections. This is the relative ease with which sound pyrolytic graphite shapes may be prepared in comparison with the difficulties encountered with pyrolytic boron nitride. Whether pyrolytic boron nitride is deposited under considerably more stress or is simply inherently more brittle is not certain, but this property is a much more sensitive function of preparative conditions in the latter than the former case. Considerable work has been done to relate the physical properties of pyrolytic graphite, such as strength and hardness, to its microstructure and thus the conditions under which it is prepared. One may expect that considerably more effort will be required in the case of pyrolytic boron nitride.

D. COMPOSITE SYSTEMS

A large number of composite systems have been the subject of exploratory investigation; the more significant are discussed here. It will be shown that successful incorporation of metals into pyrolytic structures using the halides as source materials may only occur under strongly reducing conditions while pyrolysis of certain organometallics will give carbon deposits with metallic content. In addition to the problems of chemical homogeneity, uniformity of deposition thickness, and proper choice of injector-substrate geometry previously described, these results also indicate the necessity of successful delivery of the reactants to the substrate surface in compatible concentration under conditions where preferential deposition will not occur.

1. Composites of Compounds of Hexagonal Crystal Structure

Three systems of this type have been attempted, binary composites of pyrolytic graphite, pyrolytic boron nitride, and hexagonal molybdenum carbide. In the case of pyrolytic graphite and boron nitride, two compositions were attempted, one in which the vapor composition was 1:1 benzene-B-trichloroborazole and another of 4:1. Pyrolysis was at 1600°C. Both samples were black and had the metallic luster of pyrolytic graphite. Spectrographic analysis showed a very small amount of boron to be present in each sample, while infrared spectra indicated some boron-carbon bonding. Hopefully this represents a retention of the hexagonal crystal system and not B_4C formation, a reaction which should be inoperative below 1900°C.

The cross-section photomicrograph of the 1:1 sample revealed very striking cone formation in the microstructure. Quite unexpectedly, however, it appeared that a thin layer of one pyrolytic material was first deposited preferentially, followed by a layer of the other or solution of the two, followed

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again by a resumption of the first, as indicated by three very well-defined zones. This observation was suspected to be more apparent than real, as the section was observed under polarized light, and any effect which will rotate the plane of the light will result in the appearance of a darkened zone. However, a cross-section photomicrograph of a pyrolytic sample in which first graphite and then boron nitride were deliberately deposited in successive alternate layers revealed a striking similarity.

Hexagonal molybdenum carbide, Mo_2C, is reported to have been prepared from molybdenum hexacarbonyl or molybdenum pentachloride under very careful reaction conditions as described in Section III. In exploratory experiments thus far we have been unable to obtain any evidence of the incorporation of molybdenum carbide into the pyrolytic graphite or boron nitride structure. The principal difficulty lies in the low stability of the source materials and in their premature decomposition before arriving in the vicinity of the substrate.

No product was obtained in pyrolyses until a gas flow provided by maintenance of molybdenum hexacarbonyl at 100°C was employed. X-ray examination of the small amount of product obtained showed it to be principally MoC. In addition, however, the carbonyl began to decompose at 100°C; consequently, an alternate procedure utilizing $MoCl_5$ was considered. The red-brown powder supplied by Matheson, Coleman & Bell is difficult to identify with any molybdenum-chlorine-oxygen compound. However, careful sublimation gave a small amount of green crystalline material which was assumed to be $MoCl_5$.

In only one of several runs was there any evidence of Mo_2C formation by the deposition of this $MoCl_5$ onto graphite at 1600°C. A very thin layer of white product resulted on the susceptor which shattered upon cooling and could not be recovered in sufficient quantity to be identified. In another run in which benzene and the pentachloride were pyrolyzed simultaneously, a small deposit of molybdenum metal was obtained. The formation of nonvolatile partial decomposition products before the source materials reach the susceptor was again the major reaction, an effect reported to be especially noticeable with the halides of tungsten and molybdenum.[13]

Similar experiments employing tungsten hexacarbonyl gave like results. Codeposition with benzene produced very satisfactory deposits of pyrolytic graphite which spectrographic analysis showed to contain no tungsten. As these results do not convey optimism, their priority has been greatly reduced, and future work designed to produce molybdenum and tungsten alloys of pyrolytic graphite will employ hydrogen reduction of the hexafluorides.

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2. Aluminum

As some improvement in oxidation resistance and enhancement of anisotropic structures will undoubtedly be afforded should a structure containing alternate layers of pyrolytic graphite and a metal oxide be possible, consideration was given to the deposition of metal oxides.

Anhydrous aluminum chloride (vapor pressure = 1 mm at 100°C) was passed over a graphite susceptor simultaneously as a fine stream of air was bled into the system. A very attractive deposit of alpha alumina was obtained. In a single attempt to deposit alumina and pyrolytic graphite in alternate layers, severe lamination occurred.

Attempts to pyrolyze equal molar mixtures of benzene and aluminum trichloride gave pyrolytic graphite with no appreciable aluminum content.

3. Methylcyclopentadienyl Manganese Tricarbonyl

We have proposed to prepare metal-enriched pyrolytic graphite by the vapor decomposition of organometallic compounds of the more refractory metals with high carbon content. For this purpose Ethyl Corporation's AK-33X (methylcyclopentadienyl manganese tricarbonyl), which was readily available, was considered suitable.

In the first experiment the compound was pyrolyzed at 1600°C employing a source material flow rate provided by heating the sample to 60°C, where it exhibits a vapor pressure of 1 mm. The result was amorphous carbon which X-ray fluorescence revealed contained no manganese. This deposition temperature is perhaps the lowest practical for formation of dense, well-ordered pyrolytic graphite. However, at 1600°C, metallic manganese has a vapor pressure of approximately 40 mm. Thus unless the metal is rapidly bonded into the pyrolytic structure, it would obviously distill from the heated surface. This probably accounts for the large quantity of dark by-products which thickly coated a large area of the inner surface of the vacuum system. Runs were then carried out at much lower deposition temperatures and development of the pyrolytic structure was attempted by heat treatment.

At 800°C, the formation of thin red-brown films and powders proved to have an appreciable manganese content, which was often visible as a separate phase as small metallic inclusions. Depositions at 1100°C gave identical results.

Depositions were then carried out at 1100°C employing equal vapor pressures of benzene and AK-33X. The result here was a very hard, thick, dull-red deposit with a substantial manganese content again being observed.

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Photomicrographs of the cross section of this sample revealed three details of interest. First, the sample appeared to contain various strata (though no abrupt discontinuities) with a red coloration concentrated near the surface. Second, there was a faint indication of a columnar cone structure traversing the sample vertically, and third, through the entire sample there were randomly scattered lustrous, emerald-green crystals. This is not a color associated with manganese compounds, and crystal field theory, which restricts the color which transition metal compounds may display, indicates that such a coloration would not be expected for manganese. Manganese oxide is a dull gray-green compound, and the manganate ion is dark green, almost black, but is known only in solution or as the sodium or potassium salt. In any event, oxygen was carefully excluded. This color was observed in unpolarized light, but one can detect in the cross section the presence of square-shaped pits where it appears that crystals had been cracked away in sectioning the sample, suggesting also the crystals to be present as separate entities.

In other similar runs, the green crystal formation did not occur, and it was often possible to prepare a very thin (5 mils), hard, layer of pyrolytic graphite with well-defined cone structure containing a large percentage of manganese.

The relationship between experimental conditions and the nature of the product obtained is at present not clear.

4. Boron Alloys

With regard to the discrepancy described in Section III as to the amounts of boron incorporated into the pyrolytic structures which the Bell Telephone Laboratories and the Raytheon Company have been able to achieve, a lower deposition temperature of 1600 °C was arbitrarily chosen for initial consideration of this system in order to secure a higher percentage incorporation of boron in pyrolytic graphite.

The source gases, boron trichloride and benzene, were maintained at -78 °C and -20 °C giving a 5 mm vapor pressure for each, and the deposition was made into a 3-inch diameter hemispherical graphite shell with the injector positioned 1 inch above the substrate inner, lower surface which is one of the more reliable furnace geometries for obtaining high-quality deposits. The deposit thus obtained was found to have a high boron content, a preliminary quantitative spectrographic analysis showing between 20 and 40% of the element, but owing to some incompatibility, the deposit exfoliated extensively over the entire external, and much of the internal, surface of the hemisphere (Figure 22).

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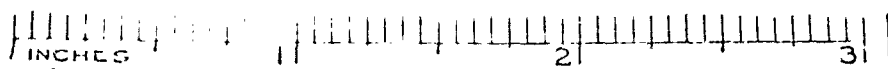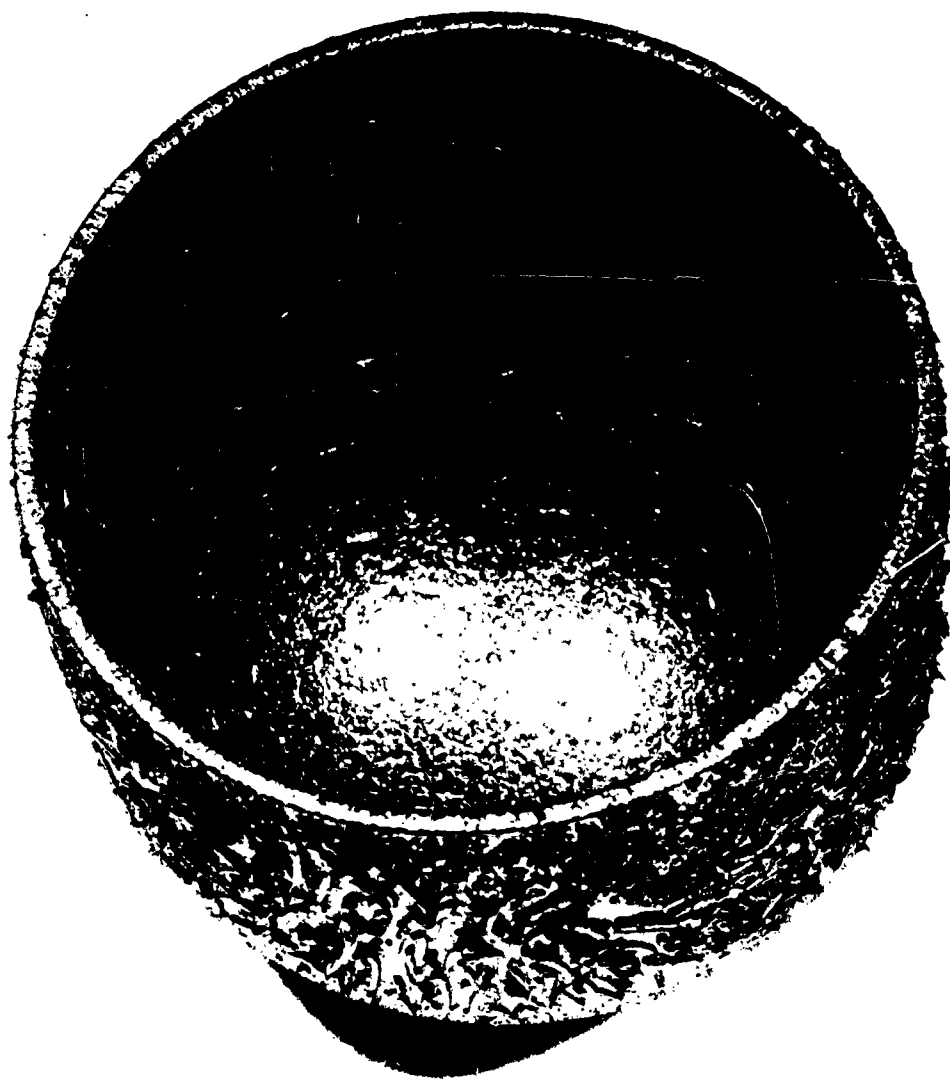
FIGURE 22   Exfoliated Deposit Produced by Simultaneous
Deposition of Benzene and Boron Trichloride

This result is reminiscent of an earlier observation on the vapor deposition of iron from iron pentacarbonyl. If a carbon content, even in trace quantities, from the following reactions:

$$Fe(CO)_5 \longrightarrow Fe + 5CO$$

$$2CO \xrightarrow[\text{catalyzed}]{\text{iron}} C + CO_2$$
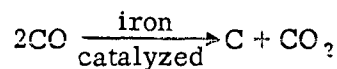
is present in the iron plate, it is not possible to achieve deposit thicknesses of more than 3 to 5 mils since the coating then curls and flakes away.

5. Dicumene Chromium

Attempts to prepare chromium pyrolytic graphite alloys at 1200°C by simultaneous deposition of dicumene chromium and benzene generally resulted in the formation of powders or thin films of chromium metal, although in one case graphite was obtained containing appreciable chromium when an argon carrier was employed.

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VI. SUMMARY

A. CONCLUSIONS

1. Massive coherent deposits of carbon and boron nitride can be deposited by the pyrolysis of hydrocarbons or boron-nitrogen compounds on graphite substrates heated at 1300°C to 2200°C.

2. The deposition is not a simple process that merely involves the production of carbon or boron nitride and hydrogen or hydrogen chloride at a hot surface, as evidenced by the formation of complex hydrocarbons and the behavior of reaction parameters.

3. The properties of the pyrolytic deposit are virtually independent of the parent gas from which they are formed.

4. The rate of pyrolytic deposition is temperature dependent and constant under given conditions.

5. The deposited carbons in pyrolytic graphite have a structure of hexagonal layer planes of carbon atoms as in graphite. The layer planes are all parallel to each other and the surface of the substrate but otherwise are randomly oriented. A similar structure is observed in pyrolytic boron nitride.

6. Essentially the same process variables prevail in either the formation of pyrolytic graphite or pyrolytic boron nitride in that lower deposition rates result in larger crystallite size, smaller interplanar distance, and higher density in the sample.

7. Pyrolytic boron nitride, in polished cross-sections, displays the cone-shaped columnar structure that is characteristic of pyrolytic graphite.

8. Pure pyrolytic graphite may be prepared with greater ease than pyrolytic boron nitride, possibly because of the volatility of pyrolysis by-products. Pyrolytic graphite appears also to be deposited with lower built-in stresses resulting in much lower brittleness and tendency to delaminate.

9. The preparation of pyrolytic graphite having a density approaching theoretical requires deposition temperatures in excess of 2000°C in sharp contrast to the 1300-1700°C observed with pyrolytic boron nitride.

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10. Pyrolytic boron nitride appears to have somewhat better resistance to erosion in oxidizing atmospheres than pyrolytic graphite.

11. Alloys of pyrolytic graphite are formed by the simultaneous deposition of a volatile metal source with hydrocarbons under strongly reducing conditions.

B. RECOMMENDATIONS

1. The field of refractory materials formed by vapor phase pyrolysis, particularly those possessing property anisotropy, is worthy of close attention. Rapidly expanding knowledge in this area will broaden their applicability as high-temperature structural materials.

2. The preparation of pyrolytic materials should be explored from a more fundamental point of view. Even though extensive investigations have been made on graphite, little information is available even on this material when formed and heat treated under closely controlled environments.

3. The continued development of methods of preparation, both of coatings and of large, sound, free-standing shapes, is essential to the realization of the utility of these materials.

4. The formation of composites of pyrolytic materials in order to obtain property enhancement is considered also to be of foremost importance, and formation of alloys of pyrolytic graphite with the more refractory metals deserves particular attention.

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VII. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data of this program are recorded in Logbooks Nos. 9525, 9526, 9694, and 9788.

Contributing personnel were:

Ronald Francis - Principal Investigator

Einar P. Flint - Project Director

Emerson H. Newton - Assistant Senior Metallurgist

D. Gordon Burgess - Assistant Inorganic Chemist

Richard W. Braman - Technician

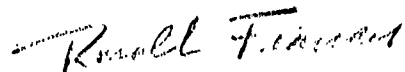James R. Aronson - Associate Inorganic Chemist

Raymond M. Cornish - Microscopist
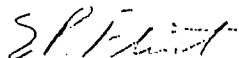
Celeste Babineau - Technician

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1961. pp. 73 - illus. 22 - tables 4, DA Project 5B92-
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Results of an experimental program devoted to the develop-
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pyrolytic techniques and furnace designs are critically evalu-
ated, and optimum conditions for the formation of pyrolytic
graphite and pyrolytic boron nitride have been investigated.
Relevant properties of pyrolytic graphite and pyrolytic boron
nitride are compared, and application of the principles de-
rived has resulted in the formation of several large sound
shapes of these materials. Exploratory experiments on the
formation of other pyrolytic systems are also described.